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# SOCIETY OF DYERS AND COLOURISTS

Volume 68 Number 8

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## Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

### LECTURES

A New Method of pH Control in Dyeing and Some Observations on the Metachrome Process
*R. J. Hannay, W. H. Major, and R. Pickin*

Recent Developments in Bleaching with Hydrogen Peroxide
*W. S. Wood and K. W. Richmond*

### COMMUNICATION

The Desorption of a Direct Cotton Dye from Cellulosic Fibres
*J. H. E. Jackson and H. A. Turner*

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# Proceedings of the Society

## The Reduction Properties of Vat Dyes

W. J. Marshall and R. H. Peters

*Meeting of the Manchester Section held in the Gas Showrooms, Town Hall Extension, Manchester, on 19th October 1951, Mr. F. Farrington in the chair*

When vat dyes are applied to textiles, they must be reduced to the water-soluble leuco form before they can be adsorbed by the fibre. Once the dye has been thus solubilised, the dyeing behaviour is similar to that of direct cotton dyes [1]. In practice, however, the dyeing of vat dyes is more difficult than the dyeing of direct dyes, and many of the additional difficulties arise in the reduction process. For example, full tinctorial value and consistent results can be obtained only if the dye is fully reduced, and to ensure this a large excess of sodium hydrosulphite is necessary. On the other hand, many vat dyes under these conditions are liable to become over-reduced, when the dye is converted into substances which cannot be reoxidised to the original dye, and such products may give rise to dull and off-shade dyeings. Hence, to obtain satisfactory dyeings, both over- and under-reduction must be avoided, and in normal usage this is accomplished by vatting each dye under the most suitable conditions of time, temperature, and hydrosulphite concentration, and then diluting so that the hydrosulphite content is diminished during the more prolonged dyeing time. The separation of the vatting and dyeing processes thus minimises the risk of over-reduction.

Unfortunately, with many methods of dyeing such a separation into two steps is not possible. In printing, the dye is reduced at the same time as adsorption occurs. In modern dyeing processes, although leuco dyeing and padding are widely used, it is often desirable to improve the penetration of the dye into the fibre, and for this purpose a common expedient is to pad the dye on to the fibre and then treat the material in a reducing bath, in which reduction and dyeing take place simultaneously. Such, for example, are the pad–steam, the Abbot–Cox, and the Standfast molten metal processes. In some of these modern methods, the time available for the processes of reduction and dyeing may be as short as 5 sec. In these cases, reduction is as much an integral part of the dyeing process as is adsorption, and it is possible for the reduction properties of the dye to have a greater influence on the final quality of the dyeing than the adsorption properties.

It is therefore desirable that full information on the reduction properties of vat dyes should be made available in order to correlate it with practical dyeing and printing behaviour. Some earlier work appears to have been carried out on this subject. Geake and his collaborators [2] have studied the reduction equilibria of a number of vat dyes, and Kienle *et al.* [3] have measured the rates of reduction of certain vat dyes under one set of conditions, while Clarke [4] has shown that an increase in temperature increases the reduction rate; but this work does not give sufficient information to demonstrate the magnitude of the differences between dyes nor to provide an overall picture of the importance of these properties. Accordingly the investigation which is reported in the present paper was undertaken to remedy the situation. The primary object was to measure the reduction properties of a fairly large number of vat dyes in order to obtain a general picture of the differences existing between them, and at the same time to correlate these properties with practical dyeing and printing behaviour.

A first step in the work was to select a method of measuring and expressing the reduction properties of a dye. Reduction, like any other chemical process, can be defined in terms of two factors, namely the rate and the equilibrium state of the reaction. Thus ease of reduction is dependent on—

(1) The maximum extent to which the reduction can be taken, i.e. the ratio of the concentrations of the oxidised and the reduced forms of the dye at equilibrium.

(2) The rate at which equilibrium is approached.

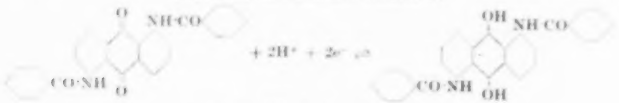
In order to make a full assessment of the reduction properties of a vat dye, it is therefore necessary to make separate measurements of each factor. One factor alone is not sufficient, and it is

important to realise that dyes which reduce rapidly are not necessarily the most fully reduced at equilibrium, and that in fact the equilibrium usually bears no relation to the rate. For the sake of convenience, however, and also because the two properties were determined separately, the two factors are treated in separate sections of the following discussion.

## The Reduction Equilibrium

A typical reduction may be represented as follows—

REDUCTION OF CALEDON YELLOW 3G



or $Ox + 2H^+ + 2e^- \rightleftharpoons RH_2$

In Acid Solution

or $Ox + 2e^- \rightleftharpoons R^{--}$

In Alkaline Solution

In the abbreviated equations above, Ox and $RH_2$ are the oxidised and reduced forms of the dye respectively.

It will be seen that the reduction of vat dyes can be considered as fundamentally a transfer of electrons, and can therefore be measured in terms of the standard oxidation-reduction potential of the system. This measurement is an established technique, in which the potential developed at a bright platinum electrode immersed in the test solution is ascertained. Experimentally such potentials can be measured in a cell of the type shown in Fig. 1, consisting essentially of a flask with three necks through which pass (*a*) the bright platinum electrode, (*b*) a reference electrode, and (*c*) a burette. A solution of the reduced dye is introduced into the cell, and then suitable amounts of an oxidising agent are added from the burette to produce changes in the ratio of the oxidised and reduced forms of the dye, the potential being measured after each addition. The electrode potential $E$ determined in this way is related to the standard redox potential $E_0$ and to the concentrations of oxidised and reduced dye and hydrogen ions by the equation—

$$E = E_0 - \frac{RT}{2F} \ln \frac{[RH_2]}{[Ox]} + \frac{RT}{F} \ln [H^+] \qquad (i)$$

where $R$, $T$, and $F$ are the gas constant, the absolute temperature, and the Faraday respectively, and the factor 2 is introduced because complete reduction involves the addition of two electrons. Thus the standard redox potential $E_0$ is a constant which is numerically equal to the potential which would be developed at the electrode in a solution of the dye containing equal concentrations of oxidised and reduced forms and unit hydrogen ion concentration. If the dye is fully dissociated, the equation may be simplified to—

$$E = E_0' - \frac{RT}{2F} \ln \frac{[R^{--}]}{[Ox]} \qquad (ii)$$

where $E_0'$ is a constant which takes into account the dissociation constants of the leuco dye.

The values of the actual potential $E$ vary with the amount of oxidising agent added, as in Fig. 2 (Curve A). The end-point of the titration corresponds to the point at which all the dye is oxidised, when the potential changes rapidly with further additions of oxidising agent. From such a titration curve, the value of the standard redox potential can be calculated using equation (*i*).

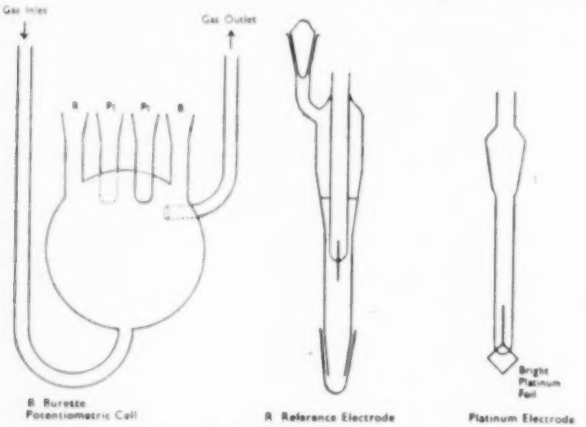



FIG. 1.—Potentiometric Titration Apparatus

The practical significance of the redox potential is that, using a standard convention, the more negative the redox potential, the more difficult is the reduction and the stronger the reducing agent necessary. Table I shows the general nature of the relation between redox potentials and reduction and oxidation processes.

The importance of redox potentials can be demonstrated by the following considerations. If two dyes with redox potentials differing by an amount $\Delta E$ are present together in a solution containing also a reducing agent sufficiently strong to bring about only 50%

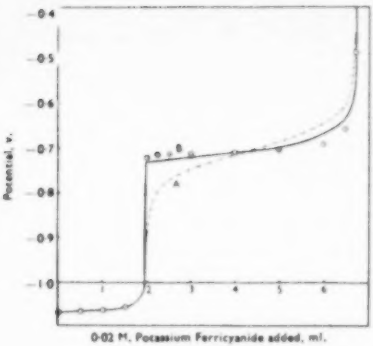



FIG. 2—Titration Curves

TABLE I

**Ease of Reduction of Oxidising Agents**

| Ease of Reduction | Redox Potential | Relative Stability of Oxidised and Reduced Forms | Examples |
|---|---|---|---|
| Strong oxidising agent (i.e. easy to reduce) | More positive | Decreasing stability of oxidised form | Potassium permanganate<br>Ceric sulphate |
| Increasingly easy to reduce | ↑ | | |
| | | Both forms stable | Ferric sulphate |
| Increasingly difficult to reduce | ↓ | | |
| Difficult to reduce | | Increasing stability of oxidised form | Quinones<br>Vat dyes |
| | More negative | | |

reduction of one of the dyes, then the extent to which the other dye is reduced may be calculated from equation (ii). At equilibrium the potentials developed by each dye and by the reducing agent are equal to that measured for the system. Thus—

$$E = E_0' - \frac{RT}{2F} \ln \frac{[R'^2]}{[Ox']} \quad \text{for the first dye}$$

$$= E_0'' - \frac{RT}{2F} \ln \frac{[R''^2]}{[Ox'']} \quad \text{for the second dye}$$

$$\therefore \Delta E = E_0'' - E_0' = \frac{RT}{2F} \ln \frac{[R''^2]}{[Ox'']} \cdot \frac{[Ox']}{[R'^2]}$$

Since the first dye is 50% reduced, $[Ox']/[R'^2] = 1$, so that—

$$\Delta E = \frac{RT}{2F} \ln \frac{[R''^2]}{[Ox'']} \qquad \text{(iii)}$$

By substituting numerical values in equation (iii) the relationship between the difference in redox potentials $\Delta E$ and the ratio of the concentrations of the reduced and the oxidised forms of the dye may be derived quantitatively, as shown in Table II.

TABLE II

**Effect of Difference in Redox Potentials on the Amount of Reduction of the Second Dye**

| $\Delta E$, v. ... | 0 | 0·028 | 0·057 | 0·100 | 0·172 |
|---|---|---|---|---|---|
| $[R''^2]/[Ox'']$* | 1 | 10 | 100 | 3000 | 1,000,000 |

* Where $\Delta E$ becomes negative, the ratio is inverted, i.e. the values refer to $[Ox'']/[R''^2]$.

From Table II it follows that a difference of only 0·05 v. in the redox potential corresponds to a change of the equilibrium reduction from 50% to 99% when $\Delta E$ is positive and from 50% to 1% when it is negative. It will be apparent, therefore, that even such small differences as 0·03 v. are significant, and a difference of 0·1 v. between the standard redox potentials of two dyes may mean that one of these dyes will be fully reduced while the other remains unreduced. In practice the oxidised forms of vat dyes are insoluble in aqueous alkali, but this merely tends to accentuate the differences which result from a given difference in the redox potentials and does not affect the general argument.

## MEASUREMENT OF REDOX POTENTIALS

Although the measurement of redox potentials is a standard technique, a great deal of care is necessary with vat dyes. To apply equation (i) both forms must be soluble, and stable potentials must be obtained after each addition of oxidising agent. The titration of the reduced form of the dye under aqueous alkaline conditions is complicated by the formation of the insoluble oxidised form of the dye. Examples of such systems have been investigated in considerable detail by Geake and his co-workers [2], who have shown that the interpretation of the electrometric titration curves is complicated by the supersaturation of the solution by the oxidised dye and the occlusion of reduced dye in the precipitated quinone. They tried to circumvent these difficulties by titrating these dyes in the presence of pyridine (0–50% was added), but further difficulties were introduced by the formation of the half oxidation products (semiquinones), the amounts of which increased with the amount of pyridine added. It is therefore preferable to work from the outset with a solvent in which both forms are soluble, and under circumstances in which no semiquinones are formed. Anhydrous pyridine is one of the few suitable solvents, and if it is acidified with hydrogen chloride semiquinone formation is prevented.

Such conditions ensure that the results obtained are a measure of a fundamental property of the dye and are not merely an arbitrary potential such as may be the case in water. Marshall and Peters [3] have indicated that the change from an aqueous medium to an organic solvent is not likely to alter appreciably the significance of the results.

## EXPERIMENTAL METHOD OF MEASURING REDOX POTENTIALS

The measurements were carried out in a cell shown diagrammatically in Fig. 1. The reference electrode was a platinum wire plated with silver and immersed in a solution of silver nitrate (0·0475 M.) in anhydrous pyridine, which gives a satisfactory reversible electrode system [4]. A saturated solution of the oxidised dye in pyridine was introduced into the cell, and also sufficient pyridine containing hydrogen chloride gas to make the hydrogen ion concentration 0·2 M. The final concentration of dye was thus governed by its solubility and by the strength of the hydrochloric

acid solution. The latter was obtained by saturating pyridine with the dry gas, and therefore its strength varied with the temperature and the atmospheric pressure. The total volume was adjusted to exactly 100 c.c.

The dye was reduced catalytically by adding a small amount (0·1 g.) of palladinised asbestos and bubbling hydrogen through the liquid. When the reduction was complete, judged by the colour change or by a trial titration, the excess hydrogen was displaced by cylinder nitrogen carefully freed from oxygen, and bubbling continued to provide agitation. (In some cases the presence of palladium interfered with the subsequent titration, and the reduction was then carried out in a separate vessel, and the reduced solution blown with nitrogen through a sintered glass disc into the titration cell.)

After about 30 min., the potentials between the bright platinum and the reference electrodes were measured with a pH meter (Cambridge Instrument Co.) at intervals of 5 min. until constant, when the titration was started by additions of a solution of anhydrous ferric chloride in pyridine from the microburette. After each addition the potential was measured until constant before a further addition was made. The strength of the ferric chloride solution used was 2 g./litre for most of the titrations, whilst in the case of the dyes whose solubility in pyridine was poor (e.g. pyranthrone) it was reduced to give a convenient titre. No attempt was made to control the concentrations of dye and ferric chloride accurately, since these titrations were carried to completion and equation (i) requires only the ratio of the two forms. The experiments were carried out at room temperature. From these potentials and the known amounts of oxidising agent added, the $E_0$ of the system was calculated by substitution in equation (i). The values of $E_0$ are referred to the working electrode, as there are no generally accepted figures on the hydrogen electrode for this solvent.

### RESULTS OF REDOX POTENTIAL MEASUREMENTS

The results for a number of dyes, listed in order of redox potential in Table III, indicate that the vat dyes show a wide range of redox potentials—from − 0·07 to − 0·49 v.,—so that their reduction equilibrium is likely to vary enormously, depending on the strength of the reducing agent used. Those at the top of the table are difficult and those at the bottom easy to reduce. To discover how the redox potentials of the dyes affect their practical properties, printing with vat dyes has been examined. If "printability" is controlled by the extent to which a dye can be reduced, it should be possible to draw a demarcation line at some potential corresponding to the power of the reducing agent used. Dyes above this line should rapidly become difficult and eventually impossible to print, whereas dyes below this line should all print fairly easily. Confirmation of this is given by the comparison of the redox potentials in column 3 and the relative ease of printing in column 4. The ease of printing was assessed on a 0–15 scale, where 15 represents rapid fixation with high tinctorial value. To make this assessment, a series of patterns was printed by the carbonate–Formosul method, in which the Formosul concentration was increased from 0 to 12% and the time of steaming was also varied. These patterns were mounted for comparison on a card and from the resultant block test, as it is called, the relative ease of printing was assessed visually. Such tests show marked differences in printing behaviour: e.g. Caledon Yellow GN gave a block of uniform colour (Fig. 3) and is an extremely good printer, whereas Caledon Pink RL gave prints (Fig. 4) which were satisfactory only with large amounts of Formosul and long steaming times, and was assessed 5 in this series. However, practical assessment of ease of printing is difficult because of the large number of variables that need to be taken into account, and this property cannot be expressed satisfactorily by a single numerical value. This difficulty of practical assessment is often the stumbling block in the correlation of physical properties and practical applications.

In Table III, the actual potential which divides the table into two parts is about − 0·25 v. Dyes with lower redox potentials print readily, while those with higher (negative) potentials print with difficulty; in fact, the two dyes at the top of the table are quite unsuitable for printing.

There is one exception—Caledon Pink RL—but the results of large-scale printing trials for this dye fall better into line with the redox potential measurements than do those from small-scale laboratory tests. Further examination shows that, whilst the dyes with potentials more positive than the critical value print in a satisfactory manner, the ease of printing does not follow the order of redox potential. This is to be expected, since the redox potential shows that they can be more or less completely reduced, and so they have all an equal chance to print. The reasons for the finer differences between the dyes in the lower half of the table are discussed later.

TABLE III

**Redox Potentials of some Vat Dyes in Anhydrous Pyridine and their Ease of Printing**

| Dye | Redox Potential $E_0$ (v.) | Relative Ease of Printing |
|---|---|---|
| Caledon Yellow 3G ... | − 0·49 | 0 |
| Caledon Brilliant Violet R | − 0·48 | 0 |
| Caledon Red 5G ... ... | − 0·40 | 1 |
| Caledon Pink RL ... ... | − 0·37 | 5 |
| Caledon Red X5B ... | − 0·36 | 2 |
| Caledon Gold Orange G ... | − 0·27 | 2 |
| Caledon Yellow 4G ... | − 0·25 | 3 |
| Caledon Jade Green XN ... | − 0·25 | 6 |
| Caledon Red BN ... ... | − 0·25 | 13 |
| Caledon Yellow GN ... | − 0·23 | 15 |
| Durindone Scarlet Y ... | − 0·23 | 10 |
| Durindone Scarlet 3B ... | − 0·22 | 10 |
| Durindone Brown G ... | − 0·22 | 12 |
| Durindone Orange R ... | − 0·21 | 8 |
| Caledon Navy Blue 2R ... | − 0·21 | 15 |
| Durindone Pink FF ... | − 0·19 | 6 |
| Durindone Red B ... ... | − 0·16 | 14 |
| Durindone Red 3B ... | − 0·11 | 12 |
| Durindone Blue 4BC ... | − 0·07 | 10 |

**Block Diagrams showing Sensitivity of Vat Dyes to Printing Conditions**

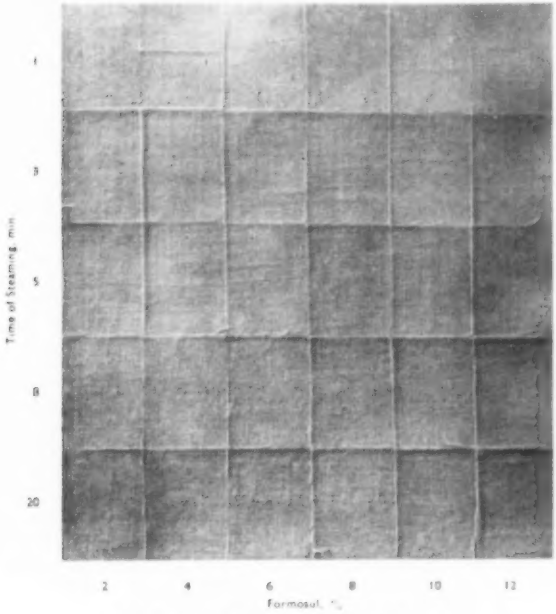



FIG. 3—10% Caledon Printing Yellow GXS Paste

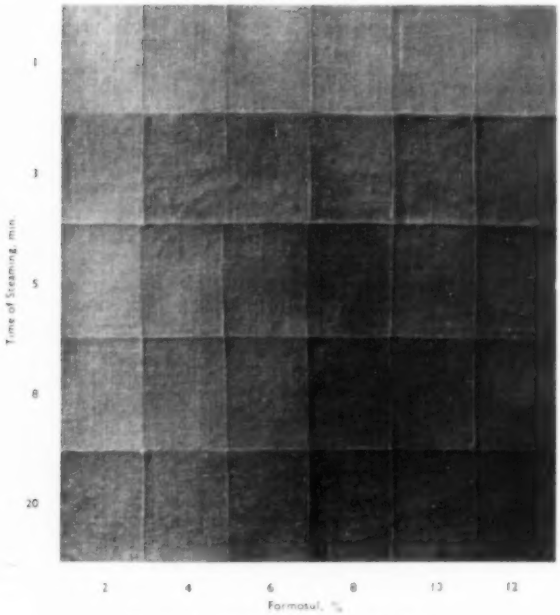
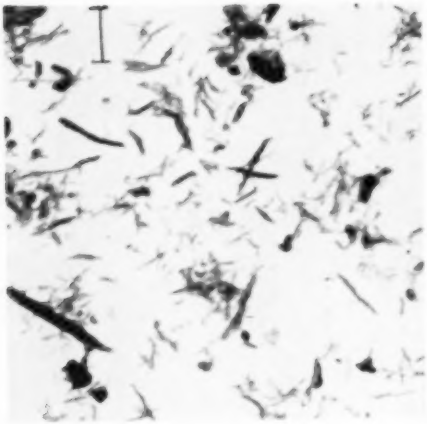



FIG. 4—15% Caledon Printing Pink RLS Paste

Scale — 1 cm. = 1 μ



$t_{1/2}$ = 5 sec.

Fig. 10.—Caledon Yellow 6X 200 Paste Fine.

$t_{1/2}$ = 50 sec.

Fig. 11.—Caledon Jade Green XN 300 Paste Fine.

**Electron Micrographs and Rates of Reduction of Particle-size Fractions of Caledon Gold Orange G**

(Scale ... 1 cm. = 2 $\mu$)

0·0·7 $\mu$.

$t_{0.5}$ = 50 sec.

FIG. 12

0·7–1·0 $\mu$.

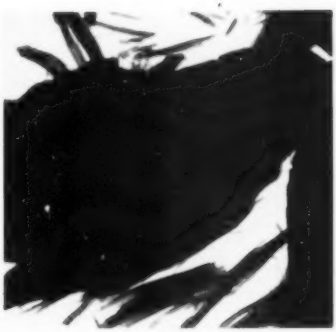
$t_{0.5}$ = 25 sec.

FIG. 13

1·3 $\mu$.

$t_{0.5}$ = 68 sec.

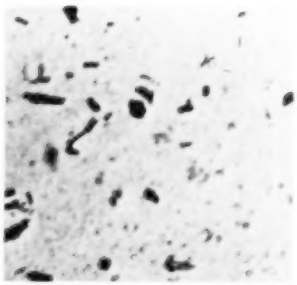
FIG. 14



3 $\mu$.

$t_{0.5}$ = 120 sec.

FIG. 15



Scale ... 1 cm. = 1 $\mu$)

$t_{0.5}$ = 283 sec.

FIG. 16— Different Preparation of Caledon Gold Orange G

### POTENTIAL MEASUREMENTS IN AQUEOUS MEDIA

Although the results in pyridine indicate that the redox potentials determine whether or not the dyes are suitable for printing, measurements in aqueous media would be more satisfactory in some ways, since the conditions are then more akin to practice. A number of dyes have been examined in aqueous alkali, and their reduction potentials measured. Since the oxidised form is insoluble in water, there is less certainty that the potentials have a real theoretical significance, and the shape of the titration curve is altered, as shown e.g. in Fig. 2, where the experimentally determined titration curve of Caledon Yellow GN in 0·1 N. caustic soda is shown by points. Curve B is the theoretical titration curve expected for this dye assuming the oxidised form to be insoluble and the leuco soluble, and it will be seen that there is good agreement with the experimental points to within a few millivolts. The titrations were carried out in the cell previously described, except that the reference electrode was changed to a normal calomel electrode and the temperature to 60°C. The dye suspension, 0·1 N. with respect to caustic soda, was introduced, and sodium hydrosulphite then added to form the leuco derivative, the total dye concentration being 0·0005 M. The potential of the bright platinum electrode was recorded, and when it became constant, oxidising agent (0·02 M. potassium ferricyanide) was added. The initial small titre at the very negative potential is due to oxidation of excess hydrosulphite, after which the potential rises abruptly to that due to the dye itself, and then increases slowly. The very abrupt rise is due to the insolubility of the oxidised form of the vat dye. For comparison the titration curve to be expected when both forms are soluble, as in redox potential measurements, is given in Fig. 2 by Curve A. A great deal of care was required to obtain satisfactory results under these conditions, and several of the dyes used, although giving satisfactory results in anhydrous pyridine, gave results which did not accord with theory in 0·1 N. caustic soda.

The equation applying to this system differs from equation (ii) only in that the concentration of the oxidised form is constant, and hence a graph of the potential *versus* the logarithm of the concentration of the reduced form should be a straight line of slope $RT/2F$. Six out of the fourteen dyes tested conformed to this theory, and these showed potentials of the same order as those obtained in anhydrous pyridine. Thus, although the interpretation of the titrations in aqueous media requires a greater number of assumptions, the results tend to confirm that the pyridine titrations do give the correct order of reducibility of the dyes under conditions more closely approaching dyeing practice. The results obtained here may be compared with those of Appleton and Geake [2], who titrated under similar conditions at 50°C. two of the dyes included here, namely Caledon Gold Orange G and Caledon Yellow GN. Unfortunately, they do not say which dyes agree with theory, and so their other results cannot be used; but if the values for the e.m.f. of the mid-point of the titration curve for these two dyes be compared at the same concentration (0·0005 M. leuco dye) and referred to a normal calomel cell (0·280 v. on the hydrogen scale), the agreement is not good. The values of Appleton and Geake become — 0·940 and — 0·672 v. respectively, compared with — 0·928 and — 0·716 v. obtained by the present authors. The latter result for Caledon Yellow GN was confirmed by two different workers using different apparatus including a different reference electrode, and the results agreed with those obtained previously by Meggy [7]. Therefore, there can be no doubt that the potential for Caledon Yellow GN is reproducible under the conditions used by the authors, and the discrepancy between their results and those obtained by Geake *et al.* is due to the difference in temperature employed (50° compared with 60°C. used here). This alters the solubilities of the oxidised forms of the dye and changes the state of solution of the leuco forms, particularly with a dye such as Caledon Yellow GN, whose absorption spectrum is given in Fig. 5 for two temperatures; such changes in

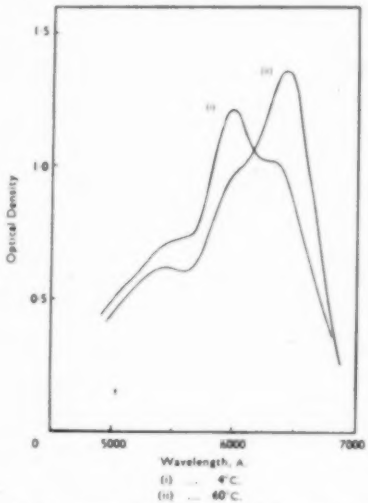



FIG. 5—Absorption Spectra of Caledon Yellow GN (leuco form)

absorption spectrum with temperature are associated with an alteration in the structure of the solute molecules, and will profoundly affect the potentials measured. When titrating Caledon Gold Orange G, the authors found that the dye was completely precipitated after 50% of the oxidising agent had been added. This is typical of semiquinone formation. The precipitate was brown in colour, and oxidised to the normal orange colour of the dye with further addition of the oxidising agent.

In the present state of knowledge of the leuco forms of these dyes, interpretations of the results obtained in this way must be treated with reserve, but the potentials obtained in pyridine solution do

not suffer from these disadvantages and have therefore been used in this work.

### REDUCTION POTENTIAL OF SODIUM HYDROSULPHITE SOLUTIONS

To form a complete picture of reducing systems it is necessary, not only to consider the dyes, but also the power of the reducing agent. Little work has been published on this matter, although Meggy and Rogers [8] have recorded some interesting attempts to measure the reducing power of print pastes by measuring the potential produced at a platinum wire electrode during printing. They found that the potential could be changed by 0·03 v. by increasing the Formosul concentration from 4 to 16%. This change is sufficient to cause a significant increase in reducing power, and the potential obtained must correspond to the critical printing potential where the line was drawn in Table III. Schaefer [9] attempted to measure the reducing power of sodium hydrosulphite in the same way, but did not correlate his results with the reduction potentials of the vat dyes. The potentials these workers obtained were undoubtedly not reversible, and so it is quite impossible to assess how much significance should be attached to them. In the present investigation the potentials produced at a platinum electrode have been measured at 60° C. for various concentrations of sodium hydrosulphite including the range used in normal vatting. In all cases, even after 6 hr., the potentials were still falling. This slow decrease was not due to a change in reducing power of the sodium hydrosulphite, for when the electrode was removed, cleaned, and replaced, the potential returned to its initial high value and then retraced its original slow fall. This is typical of irreversible systems. When the sodium hydrosulphite solution was left overnight, the potential rose by a few millivolts, suggesting a certain amount of decomposition. To obtain reproducible potentials it was found necessary to add sodium sulphite. The final potentials reached decreased with increase in sodium hydrosulphite concentration as shown in Fig. 6. These


Fig. 6.—Effect of Concentration on Potential of Sodium Hydrosulphite

potentials are 0·4–0·6 v. more negative than the potentials at which Caledon Yellow GN is reduced in water, and so are 0·1–0·3 v. more negative than those of the dyes most difficult to reduce. So, although the potentials are not thermodynamically correct, there can be little doubt that sodium hydrosulphite is a sufficiently powerful reducing agent to reduce fully all the vat dyes which have been measured. This, of course, is borne out in practice, and provided there is sufficient sodium hydrosulphite present in a dyebath, no real difficulty is encountered in reducing vat dyes fully, although reduction may be somewhat slow.

The general conclusion is that the redox potential is a measure of the reduction equilibrium of a vat dye, and is the overriding factor which determines whether or not a vat dye will print. In dyeing, however, owing to the use of a strong reducing agent, the redox potential of the dye is of little or no importance.

## The Rates of Reduction of Vat Dyes

In considering the measurement of rates of reduction, the first difficulty lies in defining the intrinsic rate of reduction of a *vat dye* as distinct from that of a *particular preparation* of a vat dye. No means of overcoming this difficulty has been discovered, and therefore it has been necessary to study several aspects of the problem, namely—

(1) The differences in rates of reduction from dye to dye and their importance in practice.

(2) The effect of changes in temperature, sodium hydrosulphite concentration, etc.

(3) The effect of the particle size of the vat dye.

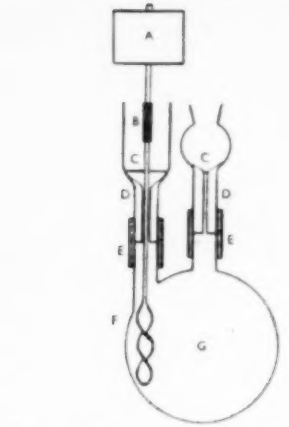
In this way it has been possible to obtain an estimate of the relative importance of the chemical constitution of the dye and of the physical condition and chemical composition of the dyebath.

### EXPERIMENTAL DETERMINATION OF RATES OF REDUCTION

In order to follow the rate of reduction of the vat dyes advantage was taken of the very great increase in optical density which occurs during reduction—the solution of the leuco dye has a much greater optical density than the suspension of the oxidised dye. The change in optical density was continuously recorded by means of the General Electric recording spectrophotometer.

The reduction reaction was carried out in a 1-cm. optical cell (Fig. 7) fitted with two capillary tubes, down one of which passed the stirrer driven by a miniature electric motor. The reducing solution was placed in the cell, and the reaction started by injecting the dye suspension through the second capillary by means of a hypodermic syringe. A few strokes of the syringe piston gave thorough mixing within 2–3 sec. The whole unit was contained in a small thermostat [10] of such a size as to fit into the cell compartment of the spectrophotometer.

In this way the reduction was followed by recording the complete absorption curve of the dye as reduction proceeded. An example is shown in Fig. 8 for Caledon Jade Green XN. Each successive curve represents an increasing amount of leuco dye, and from these curves the rate-of-reduction curve can be constructed. In practice, especially for the rapid rates of reduction, it was found better to fix the wavelength of the instrument at the peak of the absorption curve of the leuco dye and let the instrument draw directly the curve of optical density




A Electric motor
B Flexible coupling
C Liquid level
D Capillary tubes
E Rubber tubes butt-joining capillary tubes to optical cell
F Stirrer
G Flat surfaces of optical cell

FIG. 7—Rate-of-reduction Cell

against time. Fig. 9 gives a typical result for a rapid reduction. To express the rate curves obtained in this way quantitatively by a single term it is convenient to use the time of half reduction, i.e. the time taken for the concentration of leuco dye to reach half the equilibrium concentration. It has been shown[5] that the increase in optical density at any particular time is directly proportional to the amount of dye reduced, as indicated in Fig. 8 and 9.

## RESULTS

The results are given in Table IV, where each value is the mean of at least two experiments. Each dye was measured at two concentrations of caustic soda and sodium hydrosulphite and at two temperatures. The latter were chosen to correspond with vatting and dyeing practice as far as was consistent with keeping the results strictly comparable. Three conclusions may be drawn from the results in this table—

1. There are enormous differences in rates of vatting between individual dyes. For example, Caledon Yellow GN reached 50% of its final reduction in less than 5 sec., whereas Durindone Orange R took almost an hour to reach the same degree of reduction. The extreme rates thus differ by a factor of 600 times.

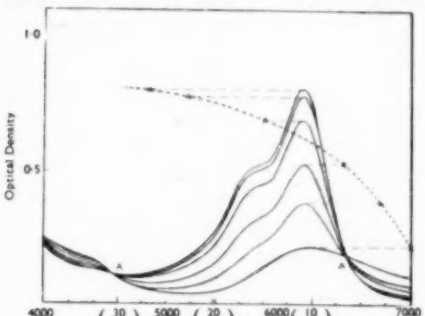
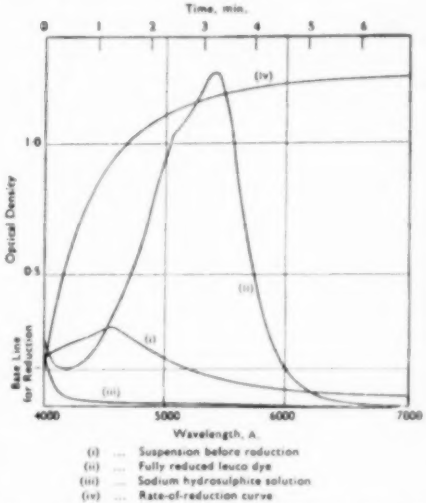



FIG. 8—Change of Absorption Spectrum on Reduction of Caledon Jade Green XN and Derivation of Rate Curve




(i) ... Suspension before reduction
(ii) ... Fully reduced leuco dye
(iii) ... Sodium hydrosulphite solution
(iv) ... Rate-of-reduction curve

FIG. 9—Absorption Spectrum Data for obtaining Rate of Reduction

TABLE IV

**Times of Half Reduction of some Vat Dyes**

(sec.)

| Temperature | 40°C. | | 60°C. | | Increase in Rate of Reduction due to— | |
|---|---|---|---|---|---|---|
| Caustic soda, g./litre | 4 | 20 | 4 | 20 | Fivefold Increase in Concn. | 20°C. Temp. Rise |
| Sodium hydrosulphite, g./litre | 4 | 20 | 4 | 20 | | |
| Caledon Yellow GN 200 Paste Fine | < 5 | < 5 | — | — | — | — |
| Caledon Red BN 200 Paste Fine | 14 | < 5 | — | — | — | — |
| Caledon Yellow 4G8 Paste Fine | 114 | 27 | — | 8 | 4·2 | 3·4 |
| Caledon Jade Green XN8 Paste Fine | 145 | 50 | — | 13 | 2·9 | 4·1 |
| Caledon Navy Blue 2R8 Paste Fine | 121 | 31 | — | 8 | 3·9 | 3·9 |
| Caledon Brilliant Violet R8 Paste Fine | 77 | 33 | — | 12 | 2·3 | 2·7 |
| Caledon Gold Orange G 200 Paste Fine | 95 | 36 | — | 15 | 2·6 | 2·6 |
| Durindone Red B8 Paste Fine | 345 | 113 | — | 54 | 3·1 | 2·1 |
| Caledon Pink RL 200 Paste Fine | 690 | 181 | — | 59 | 3·8 | 3·1 |
| Caledon Red X5B8 Paste Fine | — | 390 | 375 | 124 | 3·1 | 3·0 |
| Caledon Red 5G8 Paste Fine | 998 | 503 | — | 142 | 2·0 | 3·5 |
| Durindone Brown G8 Paste | — | 780 | — | 203 | — | 3·8 |
| Durindone Pink FF8 Paste | — | 2880 | 1620 | 660 | 2·4 | 4·4 |
| Durindone Orange R8 Paste | — | 3000 | — | 840 | — | 3·6 |
| | | | | Mean | 3·0 | 3·3 |

2. The temperature effect was similar for all dyes, a rise of 20°c. increasing the rate of reduction by a mean factor of 3·3.

3. Increasing the amounts of sodium hydrosulphite and caustic soda from dyeing to vatting concentrations increased the rate of reduction by a fairly constant factor of 3·0.

These conclusions suggest that the conditions of temperature and reducing agent will not appreciably affect the relative rates of reduction of different dyes, and thus these results should be applicable over a wide range of dyeing and printing conditions.

## Relation to Dyeing and Printing

One simple test of the practical value of the results so obtained is to see whether they can be used to interpret the empirical dyeing rules and recipes which have been accumulated in many years of experience. In normal dyeing, a concentrated stock vat is prepared with 20 g. or more of sodium hydrosulphite and caustic soda per litre, and this is subsequently diluted to the dyeing concentration. From the results of rate-of-reduction experiments, it may be seen that in this way the dye can be reduced three times more rapidly, without increasing the electrolyte concentration of the dyebath beyond that necessary to maintain reduction. Keeping down the electrolyte concentration in the dyebath makes for easier levelling and greater economy in chemicals, and reduces possible solubility troubles.

TABLE V

**Rates of Reduction and Recommended Vatting Temperatures of Vat Dyes**

| Dye | Time of Half Reduction at 40°c. (20 g. $Na_2S_2O_4$ + 20 g. NaOH per litre) (sec.) | Recommended Vatting Temperature (°c.) |
|---|---|---|
| Caledon Red BN | ~5 | 30 |
| Caledon Pink RL | (184) | (30) |
| Caledon Brilliant Violet R | 33 | 40 |
| Caledon Red 5G | (503) | (40) |
| Caledon Jade Green XN | 50 | 45 |
| Caledon Yellow 4G | 27 | 50 |
| Caledon Gold Orange G | 36 | 50 |
| Caledon Red X5B | (390) | (50) |
| Caledon Yellow GN | (~5) | (60) |
| Caledon Navy Blue 2R | 31 | 60 |
| Durindone Red B | 113 | 60 |
| Durindone Brown G | 780 | 80 |
| Durindone Pink FF | 2880 | 80 |
| Durindone Orange R | 3000 | 80 |

The vatting temperature, too, is chosen so as to achieve complete reduction within the specified vatting time. Dyes with a slow rate of vatting are vatted at higher temperatures. This is shown in Table V, where the recommended vatting temperature is compared with the rate of vatting and from which it will be seen that the lower the rate of reduction, the higher is the recommended vatting temperature. There are four exceptions, however, given in brackets. Three of these—Caledon Red 5G, Caledon Red X5B, and Caledon Pink RL—hydrolyse slightly at high temperatures, resulting in slightly off-shade dyeings, and it is to avoid this that vatting is carried out at a low temperature. In fact, it is recommended that Caledon Red 5G be vatted for a longer period than normal, presumably to compensate for the lower rate of reduction at the lower temperature. The remaining exception—Caledon Yellow GN—is vatted at a temperature higher than is necessary to give complete reduction within the prescribed time. The dyeings from this dye develop their full colour only when vatted at 60°c., and the resultant dyeing is redder than when the vat has been prepared at 30°c. This may be associated with the change which occurs in the absorption spectrum of the leuco solution when the temperature is changed, as shown in Fig. 5. These spectra indicate that there are at least two species of Caledon Yellow GN normally present in the dyebath and that the ratio of the concentrations of these compounds is altered very appreciably by a change in the temperature of the vat. There is no evidence to show what these components are, but it is known that this particular dye may be overreduced. Thus, providing there are no interfering factors, the conclusion that the choice of vatting temperature is primarily dependent on rate of reduction seems to be justified.

The real importance of the reduction properties of vat dyes becomes apparent in processes in which reduction and adsorption take place at the same time, as in printing, the pad–steam process, and the Standfast molten metal dyeing method. It has already been shown that the redox potential of the dye determines whether it will print satisfactorily or not, but tells nothing of the degree of suitability. This point may be considered further by reference to Table VI, where those dyes which appear to be satisfactory for printing on the basis of their redox potentials are tabulated in order of rate of reduction. It will be seen that the case of printing of these dyes is determined by the rate of reduction, and in fact the correlation is remarkably good. Table VII shows the same comparison for the dyes with poor printing properties, i.e. for those with redox potentials below the critical value. In this case, ease of printing bears no relation to the rate of reduction, and in fact the rates of reduction of some of the dyes in Table VII would suggest that their printing properties would be better than those of the dyes in Table VI. For example, Caledon Brilliant Violet R is not suitable for printing, although it has a time of half reduction of 33 sec. as against 780 sec. for Durindone Brown G, which prints well. It was thought that the rate of diffusion might possibly be of importance in this connection, and so the results obtained by Boulton and Morton[3] are included in Tables VI and VII where applicable. A comparison of Caledon Gold Orange G and Caledon Yellow GN, which have very similar rates of diffusion but greatly differing printing properties, suggests that diffusion rate is of little importance in this connection, so that there is little doubt that the redox potential and the rate of reduction are of primary importance in determining the printing properties of a vat dye. It follows that improvements in printing must be

sought in two directions. For dyes with low redox potentials, the reducing power of the print paste must be increased, as little improvement can be effected by increasing the rate of reduction alone. For dyes with a redox potential higher than the critical value, improvements can be obtained by methods bringing about an increased rate of reduction.

Printing has been discussed fairly fully because it gives a good example of the interplay between the rates of reduction and the redox potentials of the dyes. In modern continuous dyeing processes the rate effects must be dominant, because sodium hydrosulphite is sufficiently powerful to reduce vat dyes fully. Experiments carried out on the Standfast molten metal machine confirm this view [11].

TABLE VI

**Vat Dyes with High Redox Potential**

| Dye | Time of Half Reduction (sec.) | Redox Potential $E_0$ (v.) | Rate of Diffusion in Viscose Film ($sq.\mu$. per min.) | Relative Ease of Printing |
|---|---|---|---|---|
| Caledon Yellow GN ... | ~5 | −0·23 | 120 | 15 |
| Caledon Navy Blue 2R ... ... | 31 | −0·20 | — | 15 |
| Durindone Red B ... | 113 | −0·16 | — | 14 |
| Durindone Brown G | 780 | −0·22 | — | 12 |
| Durindone Pink FF | 2880 | −0·19 | — | 6 |
| Durindone Orange R | 3000 | −0·21 | — | 8 |

TABLE VII

**Vat Dyes with Low Redox Potential**

| Dye | Time of Half Reduction (sec.) | Redox Potential $E_0$ (v.) | Rate of Diffusion in Viscose Film ($sq.\mu$. per min.) | Relative Ease of Printing |
|---|---|---|---|---|
| Caledon Red BN ... | ~5 | −0·25 | 180 | 13 |
| Caledon Yellow 4G | 27 | −0·25 | — | 3 |
| Caledon Brilliant Violet R... ... | 33 | −0·48 | 220 | 0 |
| Caledon Gold Orange G ... ... | 36 | −0·27 | 140 | 2 |
| Caledon Jade Green XN ... ... | 50 | −0·25 | 49 | 6 |
| Caledon Pink RL ... | 181 | −0·37 | — | 5 |
| Caledon Red X5B ... | 390 | −0·36 | — | 2 |
| Caledon Red 5G ... | 503 | −0·40 | 290 | 1 |

### EFFECT OF DYEBATH VARIABLES

It having been established that the rate of reduction is of importance in printing and certain aspects of dyeing, it is necessary to determine how much control over the rate the dyer can exercise by varying the vatting conditions. In Table VIII are given the effects of changing the caustic soda, sodium hydrosulphite, and dye concentrations.

The change in reduction rate is given as a ratio of the times of half reduction. The table shows that the sodium hydrosulphite concentration has a marked effect on the rate of reduction, whilst caustic soda and dye concentrations have not. (In these experiments the conditions of measurement required the dye concentration to be much less than under dyeing conditions.) Thus the dyer can

TABLE VIII

**Effect of Concentrations of Sodium Hydrosulphite, Caustic Soda, and Dye Suspension on Rate of Reduction**

| Sodium Hydrosulphite (Caledon Gold Orange GS) | | Caustic Soda (Caledon Jade Green XN8) | | Dye Concentration (Caledon Jade Green XN 300) | |
|---|---|---|---|---|---|
| Concn. (g./litre) | Change in Reduction Rate (%) | Concn. (N.) | Change in Reduction Rate (%) | Concn. (g./litre) | Change in Reduction Rate (%) |
| 40 | 1 | 0·90 | 1·0 | 0·2 | 1·0 |
| 20 | 1·7 | 0·56 | 1·1 | 0·1 | 1·0 |
| 10 | 2·4 | 0·30 | 1·2 | 0·05 | 0·9 |
| 4 | 5·6 | 0·18 | 1·1 | — | — |
| — | — | 0·09 | 1·2 | — | — |
| — | — | 0·045 | 1·2 | — | — |

normally control the rate of reduction in two ways, namely, by changing the concentration of sodium hydrosulphite or by altering the temperature of reduction, all dyes being affected to approximately the same extent. It may be noted that in practice the concentration of caustic soda is usually increased whenever the sodium hydrosulphite concentration is increased, but the reason for this is merely to ensure that the dyebath does not become acid as the hydrosulphite decomposes.

### EFFECT OF PARTICLE SIZE

In the experiments so far described, commercial dyes were used, in which the different dyes may well differ considerably in physical form. However, electron micrographs revealed that mere particle size cannot account for the great differences in rates of reduction observed. This is illustrated by the electron micrographs of Caledon Yellow GN (Fig. 10) and Caledon Jade Green XN (Fig. 11), which show that the particle size of this particular sample of Caledon Jade Green is actually smaller than that of the yellow, and yet its rate of reduction is ten times slower. Similar observations were made on many of the other dyes.

For a more detailed study of the effect of particle size, specially prepared samples were obtained. Three dyes—Caledon Jade Green XN, Caledon Gold Orange G, and Caledon Brilliant Orange 6R—were chosen, and suitable particle size ranges prepared. The rates of reduction of all the samples were measured, and electron micrographs taken. For all three dyes the same general conclusions were reached, namely that the effect of particle size was not nearly so great as expected, but that the shape of the particle was significant. This is demonstrated in Fig. 12–15, which show the electron micrographs of four particle-size fractions prepared from the same dye suspension by centrifugal separation, with the corresponding times of half reduction. The decrease in rate of reduction with increase of particle size is very much less than would be expected if the rate were proportional to the specific surface area. The fifth micrograph (Fig. 16) is of a sample of the same dye prepared in a different way. This has a time of half reduction of 285 sec., which is much greater than that of any of the other samples, yet the

particle size is comparatively small. However, the shape of the particles in this sample differs considerably from that of the others, the axial ratio being much nearer unity. Caledon Brilliant Orange 6R also gave two types of particle, and again there was a marked difference in rate of reduction, thus confirming that the shape or crystal structure of the particle may affect reduction rate very considerably.

The reason why the rate is not proportional to the specific surface area is not known, but the larger crystals, under the influence of the reducing agent, may rapidly disintegrate into smaller particles, and may thus be reduced much more rapidly than would correspond to the size of the primary particles. There is no direct evidence for this assumption, but an apparently single crystal of Caledon Jade Green XN as seen under the microscope did not give, with X-rays, a diffraction photograph of a single crystal but rather that of a fibre [12]. Intercrystalline attack during the corrosion of metals is a well known phenomenon, and it is reasonable to expect a similar type of attack in the vat dye particle. The rate would then depend on the size of the crystal in the primary particle and not on the external surface area. Further evidence of this is shown in the electron micrographs. A close inspection of the large particles shows a tendency for them to split up into smaller, needle-like particles.

As far as the effect of the particle shape is concerned, this may be due to the relative areas of the different crystal faces. The different faces may be expected to have unequal reactivities, and so an alteration of this nature would give a change in rate of reduction.

These results are surprising, but satisfactory in that they show that the measurements made on commercial dyes are relatively insensitive to particle size variations, so that corrections for differences in size are not important. Consequently, the great differences in rates of reduction between dyes must be due to other factors, but so far no adequate explanation of the differences has been suggested. The ways in which the different dyes crystallise, the solubility of the oxidised form, and the effect of the chemical constitution of the dye on the rate at which the keto groups react with the reducing agent will all affect the reduction rate. The present results do show that the properties of the dye crystal are an important factor, but it is not yet known whether they constitute the only factor controlling the rate of reduction.

## Conclusions

The present work has demonstrated that the study of reduction processes is a very important and yet hitherto neglected aspect of vat dyeing. It has been shown that the reduction properties of vat dyes largely determine the behaviour of the dyes in printing and in many modern methods of dyeing, and may be more important in such cases than affinities and rates of diffusion, which in the past have been considered sufficient to define dyeing behaviour. In printing, the primary factor is the equilibrium state, measured by the redox potential of the dye, which determines whether or not the dye will print. Further differentiation between dyes is then dependent on their rates of reduction. In dyeing, the use of a reducing agent which is much stronger than that commonly employed in printing leads to the complete reduction of all vat dyes at equilibrium, so that the rate of reduction alone is important in determining dyeing behaviour. It has also been shown that the effect of the particle size of the vat dye suspension on rate of reduction is small as compared with the differences existing between different dyes, which are very great.

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## Discussion

Mr. F. FARRINGTON: Presumably the remarks on ease of fixation in printing refer to the normal potash–Formosul recipe. Examples of dyes other than Caledon Yellow 4G which do not print by the normal potash recipe but give completely satisfactory results in the presence of strong caustic soda are Caledon Blue RS and Caledon Brown RS, and it would be interesting to know their redox potentials. Neither of these printing processes is applicable to Caledon Blue RC, and yet this dye gives excellent yields when printed by the Jeanmaire process. In other words, many factors other than redox potential are involved in the fixation of vat printing dyes.

Mr. MARSHALL: It is quite true that the printing referred to in the paper was by the normal potash–Formosul recipe. According to our argument the reducing power of the print paste determines which dyes can be printed by that method. If addition of caustic soda should increase this reducing power, then the range of printable dyes will be extended by such addition. We have not carried out any work to determine the effect of caustic soda on the reducing power of either hydrosulphite or Formosul in printing pastes. Presumably the two dyes mentioned are borderline cases and their redox potentials are in the region more negative than those dyes which print satisfactorily by the potash–Formosul method. In this paper we have considered only the reducing power of the dyes, and no doubt many other factors are operative in their printing. In particular we might expect that the

solubility, the dissociation constant of the leuco acid, complex formation with the paste thickening, and the rate of diffusion into the fibre will all be of some importance in determining the overall printing properties of the dyes.

Mr. H. A. TURNER: Have the authors obtained any evidence which would suggest that the presence of the vat dye itself modifies the reduction potential of the hydrosulphite?

Dr. PETERS: We have not tried measuring the potential of hydrosulphite directly in the presence of the vat dyes, but we have carried out some experiments on adding various anthraquinones (anthraquinone, "silver salt"*, and anthraflavic acid) to hydrosulphite and following the potential developed. It was found that a steady potential was reached only in the case of anthraflavic acid within 5 hr., and we came to the conclusion that these additions merely affected the rate at which the final potential was approached, but that the final potential itself was substantially independent of the additives. Similar results were obtained during the titration of vat dyes reduced in aqueous solution by hydrosulphite. Thus we may conclude that the presence of the vat dye itself will modify the reduction properties of hydrosulphite only in respect of the rate, but that the potential reducing power is probably little affected.

Mr. C. P. ATKINSON: It would be interesting to have further observations as to the effect of temperature, in view of the conditions of application of vat dyes by the molten metal process, and also the "flash reduction" procedure at temperatures exceeding 212° F. which is stated to be a feature of the continuous hot oil process.

Mr. MARSHALL: Measurements of the rates of reduction of vat dyes at the higher temperatures used in the processes mentioned would be of considerable interest. Unfortunately, these cannot be carried out with the present apparatus, because of the very high rates of reduction involved, and in addition, the optical glassware used would not withstand the higher temperatures. Thus full tinctorial value of a pigment-padded vat dye can be obtained in 7 sec. at 85°C. in the Standfast molten metal machine, so that, for 50% of the vat dyes (the proportion which can be satisfactorily developed in this time), absorption, in addition to full reduction, is attained in this period. This corresponds to a time of half reduction of less than one second. This type of measurement would require special techniques to enable the complete mixing of the reagents to be accomplished within a small fraction of a second. The rate itself would require to be measured by such a technique as cathode-ray oscilloscope photography, and could certainly not be undertaken with the Hardy instrument used in the experiments described in the paper.

* Sodium anthraquinone-β-sulphonate

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COMMUNICATIONS

# The Reaction between Wool and Nickelammonium Hydroxide

## I—The Adsorption of Nickel by Wool from Solutions of Nickelammonium Hydroxide

J. W. BELL and C. S. WHEWELL

When wool is placed in solutions of nickelammonium hydroxide, nickel is taken up, the amount and rate being affected by the concentration of the reagent, the time, and the temperature. The maximum amount adsorbed is 22%, but the total weight increase is greater than that which would be expected from union with nickel alone. There is, however, no increase in nitrogen content, and it is suggested that, when nickelammonium hydroxide combines with wool, there is interchange between the coordinated $NH_3$ groups and the >NH groups in the main chains. In presence of ammonia some $NH_3$ groups are also coordinated with the combined nickel, but these change on washing to –OH or $H_2O$. In agreement with this view, modification of the disulphide or the salt linkings has little effect on the total amount of metal finally taken up.

It has been shown by Whewell and Woods[1] that, when wool is immersed in a solution of cuprammonium hydroxide, copper is adsorbed and the fibre contracts in length. Subsequent treatment with sulphuric acid removes the copper and causes the fibre to return, wholly or partly, to its original length. It has now been found that wool reacts with nickelammonium hydroxide; the fibres are coloured reddish brown owing to the adsorption of nickel, and they also contract. The object of this communication is to give an account of a detailed study of the reaction between wool and the nickelammine.

### Experimental

#### PREPARATION OF REAGENTS

WOOL—Lincoln wool was used throughout the investigation. Locks were taken from a freshly clipped fleece, and the tip half of each lock was cut away. The root portions were then cleaned by successive extractions with ether and alcohol followed by thorough washing first in tap water and finally in distilled water, particles of dirt and other impurities being removed by hand. The material was allowed to dry at room temperature.

NICKELAMMONIUM HYDROXIDE—In the early stages of the work, the reagent was prepared by shaking together for four days in a rotary shaker batches of 20 g. of powdered salt-free nickel hydroxide and 700 ml. of ammonia solution (sp. gr. 0·880). The blue solution formed contained about 5 g. of nickel per litre, and was freed from suspended nickel hydroxide by decantation and filtration. Later the following, more satisfactory method was adopted—

Approx. 50 g. of finely powdered metallic nickel

was vigorously stirred in 700 ml. of concentrated ammonia solution containing about 3 g. of sucrose, a stream of air saturated with ammonia vapour being passed through the liquid. After a comparatively short time (4–8 hr.) blue solutions containing 15–20 g. of nickel per litre were obtained. Prolongation of the reaction led to decomposition of the solution and precipitation of nickel hydroxide. Excess nickel powder was removed from the solution by decantation and filtration. All solutions were stored in an ice chest to minimise the possibility of decomposition.

### ANALYTICAL METHODS

ESTIMATION OF NICKEL IN SOLUTIONS—The solutions of nickelammine were diluted with water and boiled to decompose the complex and remove ammonia. Precipitated nickel hydroxide was dissolved in a slight excess of sulphuric acid, and the amount of nickel in the solution determined by precipitation of nickel dimethylglyoxime from slightly acid solutions, using the technique described by Vogel[2].

ESTIMATION OF AMMONIA—Ammonia was determined by acidifying the solution with standard 4 N. sulphuric acid and back-titrating the excess acid with standard N. sodium hydroxide using methyl red as indicator. The acid used up combines with free ammonia, with ammonia in the complex, and with the nickel itself. Once the concentration of nickel is known, a correction can be applied to account for the acid taken up by the nickel. There is some doubt, however, as to whether the nickel complex contains four or six co-ordinated ammonia groups, and consequently it was convenient to calculate only the sum of the free and combined ammonia.

ESTIMATION OF NICKEL COMBINED WITH THE FIBRE—This may be carried out either by analysing the solution before and after treatment or by direct analysis of the nickel-containing wool. In the first method an allowance must be made for the amount of water introduced into the reagent solution along with the wetted and centrifuged wool sample. With dilute solutions this procedure is satisfactory provided the wool is not too severely degraded, but errors arise if the solution contains protein, as the precipitate of nickel dimethylglyoxime then contains substantial amounts of occluded material. Difficulties arise when wool is treated with more concentrated solutions, as the concentration falls only slightly when nickel is taken up by the wool. In these cases, therefore, it was found necessary to determine the nickel content of the treated wool itself. The following procedure was finally adopted—

After the treated wool had been removed from the liquor, it was transferred rapidly to a centrifuge tube and centrifuged for 2 min. to remove excess reagent. The wool was then weighed to determine the amount of liquor still retained, thus providing data to make a correction for nickel present in the occluded liquor. Nickel was then estimated by rinsing the sample with dilute sulphuric acid and analysing the wash liquors by precipitation with dimethylglyoxime in the usual way.

## Results

### ADSORPTION OF NICKEL BY UNTREATED WOOL

The adsorption of the nickel is affected by the time of reaction between the wool and the nickel-ammonium hydroxide, the initial concentration of the nickel solution, the concentration of ammonia, and the temperature. The relevant data are summarised in Tables I–III.

TABLE I

**Effect of Nickel Concentration on Adsorption**

(Ammonia concn. 240 g./litre. 0°C. Liquor ratio 100 : 1)

| Nickel Concn. (g./litre) | Nickel adsorbed (%) after (hr.)— 0·5 | 1 | 2 | 3 | 4 | 6 | 8 | 12 | 16 | 24 | 71 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *2·1 | — | — | 1·8 | — | 3·3 | 5·0 | 7·4 | 9·0 | 9·5 | — | — |
| 2·5 | — | — | 3·7 | 4·7 | — | — | 7·8 | — | 9·9 | 10·5 | 10·8 |
| *3·1 | — | — | 3·0 | — | 5·8 | 8·4 | 9·4 | 11·3 | 12·2 | — | — |
| *4·1 | — | — | 5·6 | — | 9·5 | 12·0 | 12·9 | 13·5 | 14·5 | — | — |
| 5·0 | — | — | 7·2 | — | 9·9 | — | 12·7 | — | 15·3 | 17·6 | 17·4 |
| 10·0 | 4·1 | 10·3 | 14·5 | 17·1 | 18·6 | 20·2 | 20·6 | — | 21·6 | — | — |
| 15·0 | 4·4 | 9·8 | 15·4 | 17·5 | 19·0 | 20·4 | 21·0 | — | 21·1 | 21·1 | — |

* Solutions prepared by shaking nickel hydroxide with ammonia. The remaining solutions were prepared from powdered nickel.

TABLE II

**Effect of Ammonia Concentration on Nickel Adsorption**

(Ni concn. 5 g./litre*. 20°C. Liquor ratio 100 : 1)

| Concn. of Ammonia (g. $NH_3$ per litre) | Nickel adsorbed (%) after (min.)— 15 | 30 | 45 | 60 | 90 | 120 | 240 |
|---|---|---|---|---|---|---|---|
| 270 | 8·0 | 14·4 | 17·2 | 18·6 | 19·2 | 19·0 | — |
| 245 | 9·8 | 13·1 | 15·2 | 16·4 | 17·6 | 18·1 | 19·0 |
| 225 | 8·5 | 11·8 | 14·1 | 15·1 | 16·6 | 17·4 | 18·5 |
| 200 | 7·4 | 10·8 | 12·9 | 14·2 | 15·4 | 17·1 | — |
| 170 | 7·9 | 11·5 | 13·1 | 14·0 | 15·8 | 16·9 | 18·0 |
| 150 | 6·8 | 9·2 | 10·5 | 11·8 | 13·0 | 14·2 | 16·6 |
| 100 | 6·0 | 8·9 | 9·7 | 10·8 | 11·8 | 13·0 | 14·9 |
| 68 | 7·6 | 9·6 | 10·8 | 11·5 | 12·7 | 13·6 | 15·7 |

*Most of the solutions were prepared from a stock solution of nickelammonium hydroxide by diluting with the appropriate amounts of water and 0·880 ammonia, but those containing more ammonia than the stock solution were prepared by bubbling in ammonia gas.

It is clear from Table I that the concentration of the solution has a great effect not only on the rate of reaction but also on the maximum adsorption obtained. With a solution containing 2·1 g. of nickel per litre, 10% adsorption is attained after 16 hr. at 0°C. When solutions containing 5 g. of nickel per litre are used at 0°C. a maximum adsorption of 18·5% is indicated by extrapolation. In both instances a considerable amount of nickel remains in solution. When using solutions containing 10 and 15 g. of nickel per litre, however, particularly at 20°C. and 30°C., a maximum adsorption of around 22% of nickel is reached in several different experiments. This suggests that 22% of nickel is indeed the maximum amount the wool can adsorb.

The maximum adsorption may also be determined by measuring the adsorption from solutions of various concentrations and extrapolating to find the take-up from an infinitely concentrated solution. It can be seen from Fig. 1 that for a solution of infinite nickel concentration the equilibrium adsorption by the wool would be about 25%.

TABLE III

**Effect of Temperature on Nickel Adsorption**

(Ammonia concn. 240 g./litre. Liquor ratio 100 : 1)

| Time of Treatment (hr.) | Nickel adsorbed (%) from Solutions of Nickel Content (g./litre)— 2·5 | 5·0 | 10·0 | 15·0 |
|---|---|---|---|---|
| | TEMPERATURE 0°C. | | | |
| 0·5 | — | — | 4·1 | 4·4 |
| 1 | — | — | 10·3 | 9·8 |
| 2 | 3·7 | 7·2 | 14·5 | 15·4 |
| 3 | 4·7 | — | 17·1 | 17·5 |
| 4 | — | 9·9 | 18·6 | 19·0 |
| 6 | — | — | 20·2 | 20·4 |
| 8 | 7·8 | 12·7 | 20·6 | 21·0 |
| 16 | 9·9 | 15·3 | 21·6 | 21·1 |
| 24 | 10·5 | 17·6 | — | 21·1 |
| 71 | 10·8 | 17·4 | — | — |
| (min). | TEMPERATURE 20°C. | | | |
| 5 | — | — | 4·9 | — |
| 10 | — | — | 12·5 | — |
| 15 | 3·7 | 8·4 | 16·6 | 17·2 |
| 20 | — | — | 19·6 | 19·8 |
| 30 | 6·8 | 11·5 | 20·0 | 21·0 |
| 45 | 8·4 | 13·6 | — | 21·3 |
| 60 | 9·8 | 15·2 | 21·6 | 21·9 |
| 90 | 11·1 | 16·0 | — | 21·9 |
| 120 | 11·8 | 17·4 | — | 21·9 |
| 240 | 12·9 | 17·0 | — | 22·0 |
| | TEMPERATURE 30°C. | | | |
| 5 | 4·1 | 6·1 | 14·1 | 16·1 |
| 10 | 6·3 | 10·6 | 18·6 | 20·3 |
| 15 | — | 13·2 | 20·9 | 21·2 |
| 20 | 8·6 | 15·2 | 21·7 | 21·8 |
| 30 | 10·2 | 17·5 | 22·2 | 22·1 |
| 45 | 11·6 | 18·3 | 22·4 | — |
| 60 | 12·4 | 18·3 | 22·3 | — |

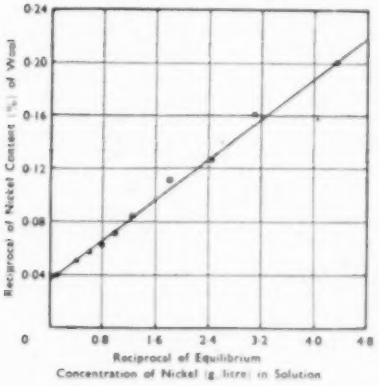


FIG. 1

KINETICS OF THE REACTION—If the rate of reaction between wool and nickelammonium hydroxide is governed by the rate of penetration of reagent into the fibre, then for any adsorption isotherm a plot of the square root of time against the amount of nickel adsorbed will be linear [3]. Examination of a number of adsorption–time curves indicated clearly that this relationship was not valid.

The reaction is not markedly dependent on the speed at which the wool is moved in relation to the solution, which suggests that liquid diffusion is not a rate-determining factor. This view is supported by consideration of the more detailed treatment used by Vickerstaff [4].

Unless the adsorption of nickel exceeds about three-quarters of the equilibrium value, the relation between $t$ and $\log (a - x)$ ($t$ = time of reaction, $a$ = equilibrium adsorption of nickel, and $x$ = adsorption after time $t$) is expressed by a straight line (Fig. 2), which suggests that the reaction is apparently of the first order. By applying the

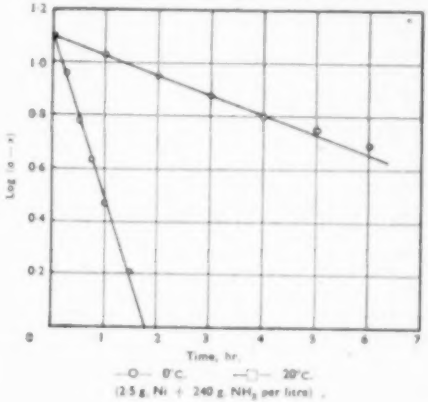


FIG. 2

Arrhenius equation to the data obtained at 0°, 20°, and 30°C., values for the heats of activation were obtained (Table IV).

TABLE IV

**Heats of Activation**

(kg. cal.)

| Concn. of Ni in Soln. (g./litre) | 0–20°C. | 20–30°C. |
|---|---|---|
| 10 | 20·65 | 11·85 |
| 5 | 23·25 | 13·40 |
| 2·5 | 17·35 | 14·30 |

The values are clearly dependent on both the concentration of the solution and the temperature at which the reaction is carried out, but are comparatively low. Values for true chemical reactions are about 50 kg.cal., and this would suggest that the controlling reaction to which the above figures refer is one involving a looser union, such as co-ordination valencies.

### ADSORPTION OF NICKEL BY CHEMICALLY MODIFIED WOOLS

When wool is immersed in nickelammonium hydroxide and the nickel is taken up, it is possible that it combines with the wool through the various active groups in the fibre. It would be expected, therefore, that the adsorption of nickel by chemically modified wool would be different from that by unmodified material. The purpose

of the following experiments was to find out whether this is, in fact, so, and to obtain some information on the particular groups which are of importance in determining the uptake of nickel.

(*a*) MODIFICATION OF AMINO GROUPS—The well known van Slyke method of deaminating wool [5] by the action of nitrous acid was considered unsuitable. There is a possibility that the disulphide links may be broken and that new hydroxyl groups may be as reactive as the amino groups they have replaced. The method of blocking amino groups by dinitrofluorobenzene was preferred [6].

Dinitrofluorobenzene (DNFB) was prepared by the method of Cook and Saunders [7], and the reaction with wool carried out as follows—2 ml. of DNFB was dissolved in 100 ml. of ethyl alcohol, and to this was added a solution of 2 g. of sodium bicarbonate in 50 ml. of water. A precipitate of excess bicarbonate appeared, but was allowed to remain, as it does not interfere. A 2-g. sample of wool was heated in this solution for 48 hr. at 40° C., and thoroughly rinsed first in tap water, then in ethyl alcohol, and finally in distilled water.

(*b*) MODIFICATION BY ACETYLATION—Two 2-g. lots of wool were acetylated by boiling under reflux with acetic anhydride for 30 min. and 4 hr. respectively, and then thoroughly washing in water. According to Blackburn and Phillips [8], acetylation for 30 min. introduces 12·6% of acetyl groups into the wool, 2·2% being *O*-acetyl and the remainder *N*-acetyl. Treatment for 4 hr. increases the acetyl content to 14·8%, 2·8% of which is *O*-acetyl. It is clear, however, that 4-hr. acetylation damages the wool severely. Fibres contract as much as 10% in length and become weak and brittle, and it appears probable that side-reactions, other than acetylation of amino and hydroxyl groups, take place.

(*c*) MODIFICATION OF THE DISULPHIDE LINKING BY CONVERSION TO LANTHIONINE—Wools modified in this way were prepared (i) by immersing a 2-g. sample of wool overnight at 20° C. in 1 litre of 0·1 N. sodium hydroxide and (ii) by immersing a 2-g. sample of wool for 24 hr. at 60–65° C. in 0·1 N. potassium cyanide. Both samples were then thoroughly rinsed in distilled water. Treatment of wool with sodium hydroxide solution converts about half the disulphide bonds to lanthionine (–C·S·C–) cross-linkings [9], and a more complete conversion is effected by potassium cyanide [10].

(*d*) MODIFICATION OF THE DISULPHIDE LINKING BY INTRODUCTION OF A METAL—A 2-g. sample of wool was immersed at room temperature in 200 ml. of a solution of 0·1 N. mercuric acetate and 0·1 N. acetic acid for 15 hr., after which time it was removed and rinsed thoroughly in distilled water. It appeared to be considerably damaged. The exact nature of the reaction between mercuric acetate and wool has not been established [11], but it is probable that cross-linking occurs which involves the disulphide bonds and converts some of them to –S·Hg·S–.

(*e*) MODIFICATION BY METHYLATION—Wool was methylated according to the procedure of Blackburn, Carter, and Phillips [12]. A 2-g. sample of wool was agitated with a mixture of 0·4 ml. of methyl sulphate and 0·7 g. of sodium acetate dissolved in 30 ml. of water. After 90 min., a further 0·4 ml. of methyl sulphate and 0·7 g. of sodium acetate were added. Similar additions of methyl sulphate and sodium acetate were made at intervals of 90 min., the total time of reaction being 12 hr. After removal from the reagent the wool was rinsed overnight in running water and finally in several changes of distilled water. Blackburn *et al.* consider that the methylation is confined largely to the carboxyl groups, though some *N*-peptide methylation may also take place.

(*f*) MODIFICATION BY METHYLATION AND ACETYLATION—Wool was immersed for 20 hr. at room temperature in a 10% solution of acetic anhydride in methyl sulphate [8]. By this method methyl groups are introduced and acetylation also occurs, though not to the same extent as in refluxing with acetic anhydride.

Values of nickel adsorption by these chemically modified wools are summarised in Table V.

TABLE V

**Nickel adsorbed (%) by Chemically Modified Wools**

(10 g. Ni = 240 g. $NH_4$ per litre at 20° C. and liquor ratio 100 : 1)

| Time (min.) | No Treatment | DNFB | Acetylation 30 min. | Acetylation 4 hr. | NaOH – KCN | Mercuric Acetate | Methyl Sulphate | $(CH_3)_2SO_4$ + $(CH_3CO)_2O$ |
|---|---|---|---|---|---|---|---|---|
| 3 | — | — | — | — | 12·2 | 13·8 | — | — | — |
| 5 | 4·9 | 6·0 | 10·9 | 14·7 | 14·0 | 15·7 | 1·1 | 6·6 | 2·8 |
| 10 | 12·5 | 9·3 | 17·7 | 15·2 | 16·2 | 18·9 | 2·7 | 11·7 | 8·6 |
| 15 | 16·6 | — | — | — | 17·4 | — | 6·1 | — | — |
| 20 | 19·6 | 14·0 | 19·3 | 15·3 | — | — | 14·5 | 18·1 | 17·4 |
| 30 | 20·0 | 14·6 | 19·7 | 15·3 | 18·6 | 19·7 | 18·6 | 19·5 | 19·9 |
| 45 | — | — | 19·7 | 15·1 | — | — | — | — | — |
| 60 | 21·6 | 8·4 | 19·9 | 15·2 | 19·8 | 20·2 | 20·2 | 20·9 | 21·5 |
| 90 | — | 14·4 | 19·6 | 15·1 | — | — | — | 21·0 | 22·4 |
| 120 | — | 19·4 | — | — | — | 20·9 | 20·1 | — | — |
| 240 | — | 22·6 | — | — | — | — | — | — | — |

*Discussion*

Modification of wool with dinitrofluorobenzene greatly increases what may be termed the induction period of the reaction, but once adsorption of nickel has begun it proceeds in a manner very similar to that with unmodified wool. The salt-link amino groups therefore play only a secondary part in the reaction and have no influence on the maximum adsorption of nickel. It is possible that the first reaction of the strongly alkaline nickelammonium

hydroxide solution is one of salt-link back titration, thus causing fibre swelling and making other sites available for combination with nickel. There are, for example, sufficient peptide nitrogen groupings available to account for the 22% adsorption in terms of a nickel–nitrogen co-ordination reaction. It was noted during the experiment that dinitrofluorobenzene-modified wool swells much more slowly in nickelammonium hydroxide than does unmodified wool. This reduction in swelling might arise from steric hindrance caused by the presence of dinitrophenyl residues.

Modification of the disulphide linkings by treatment with caustic soda and potassium cyanide leads to an increase in the initial rate of nickel adsorption, but has little effect on the equilibrium adsorption value. These pretreatments, besides converting some disulphide linkings into lanthionine linkings, cause damage and degradation to the wool fibre and probably increase the susceptibility to swelling, thus giving a greater rate of adsorption. It seems unlikely, however, that the disulphide linkings are of importance as sites for nickel adsorption. The effect of providing more cross-links is shown by the mercuric acetate modification. In spite of evident degradation, which might be expected to increase the rate of adsorption of nickel, the uptake is retarded, although the maximum amount adsorbed is not greatly affected. Again, therefore, it may be inferred that the sites of reaction have not been inactivated.

To boil wool in acetic anhydride is a drastic treatment, which obviously causes severe damage, and it is no doubt owing to this that the adsorption of nickel is accelerated. A four-hour acetylation, however, results in a marked decrease in the equilibrium adsorption, which suggests that acetylation has diminished the number of sites available for combination.

Modification by methylation with and without simultaneous acetylation has little effect on either the rate of uptake of nickel or the maximum adsorption. It appears unlikely, therefore, that the carboxyl groups are sites of reaction with nickel. If, as has been suggested, some peptide nitrogens have been methylated, then either these particular sites are not involved or the introduction of a methyl group has not impaired their co-ordinating powers.

### COMBINATION BETWEEN WOOL AND NICKEL

As modification of amino, phenolic, carboxyl, and disulphide groups has little effect on the equilibrium adsorption of nickel, it is likely that the main-chain >NH or >CO groups are involved, and that union of the nickel through co-ordinated valencies is a possibility. In nickelammonium hydroxide the nickel atom is co-ordinated with four or six $NH_3$ groups, and all or some of these may be exchanged for NH groups in the wool. To determine whether the nickel adsorbed is associated with attached $NH_3$ groups, the nitrogen contents of wools treated with nickelammonium hydroxide, and also those of the samples after the adsorbed nickel had been removed, were estimated by the Kjeldahl method (Table VI).

TABLE VI

**Nitrogen Content of Wool treated in Nickelammonium Hydroxide**

(5 g. Ni : 240 g. $NH_3$ per litre, 2°C., Liquor ratio 10:1)

| Time of Treatment (min.) | Nickel Content of Wool (%) | Nitrogen Content of Wool (%) — Containing Nickel | After Removal of Nickel |
|---|---|---|---|
| 0 | 0·0 | 15·9 | 15·9 |
| 15 | 8·4 | 16·2 | 16·1 |
| 30 | 11·8 | 16·7 | 15·5 |
| 120 | 17·6 | 16·2 | 16·0 |

Clearly there is no increase in nitrogen content, and this suggests that the exchange is complete. There remains the possibility that the nickel combines initially in the form of a nitrogen-containing complex radical, which is hydrolysed during aqueous rinsing. In Table VII the nitrogen content of nickel-containing wool which has been rinsed only in absolute alcohol is compared with that of nickel-containing wool given an aqueous rinse.

TABLE VII

**Nitrogen Contents of Wool rinsed in Alcohol and Water**

(1 hr. in 10 g. Ni + 240 g. $NH_3$ per litre at 2°C. and 100 : 1 liquor ratio)

| Treatment | Nickel Content (%) | Nitrogen Content (%) |
|---|---|---|
| No treatment ... ... ... | — | 15·9 |
| Nickelammonium hydroxide followed by rinsing in absolute alcohol ... ... ... ... | 18·5 | 21·6 |
| Nickelammonium hydroxide followed by rinsing in absolute alcohol and finally in water... | 17·5 | 13·1 |

These results indicate that a fall in nickel content from 18·5 to 17·5% is accompanied by a considerable reduction in nitrogen—from 20·6 to 16·1%. This is much too great to be accounted for by the removal of a nitrogen–nickel complex as a whole. It appears that in the initial combination with wool the nickel is attached to a co-ordinated $NH_3$ group. The adsorption of 20% of nickel associated with one $NH_3$ group per nickel atom would in fact increase the nitrogen content from 16% to 20·8%, which compares well with the experimental increase of 4·5%. Aqueous rinsing, therefore, either alters the co-ordination number of the nickel or replaces the ammonia by a water molecule.

### CHANGE IN WEIGHT OF WOOL TREATED IN NICKELAMMONIUM HYDROXIDE

If the adsorbed nickel is attached to co-ordinated ammonia or water molecules, then the increase in weight due to adsorption should be greater than the simple uptake of nickel. This was shown to be so (Table VIII) by treating samples of known dry weight for various times with nickelammonium hydroxide and measuring the uptake of nickel and the change in dry weight. All the samples were rinsed in aqueous ammonia (0·880), centrifuged, and rinsed in alcohol.

The same conclusions may be drawn from a series of experiments in which samples of wool, each weighing 212·1 mg. when dry, were treated for

TABLE VIII

**Increase in Weight on Treatment with Nickelammonium Hydroxide**

(Original dry weight of each sample 105·9 mg.)

| Increase in Weight (mg.) | Nickel Content (mg.) | Non-nickel Increase (mg.) |
|---|---|---|
| 6·0 | 3·4 | 2·6 |
| 9·3 | 6·9 | 2·4 |
| 13·8 | 8·9 | 4·9 |
| 17·5 | 12·6 | 4·9 |
| 21·2 | 13·9 | 7·3 |
| 26·2 | 18·3 | 7·9 |
| 28·7 | 20·4 | 8·3 |

different times in nickelammonium hydroxide. After removal from the solution, all samples were rinsed first for 5 sec. in concentrated ammonia (0·880), and then for 6 hr. in several changes of distilled water, before being conditioned in the laboratory for 24 hr., and dried to constant weight over phosphorus pentoxide *in vacuo*. From these data it is possible to calculate the total increase in weight due to the treatment. The amount of nickel in the samples was determined in the usual way. Results are recorded in Table IX, which includes the theoretical weight increase on the basis of one water molecule per nickel atom.

TABLE IX

**Experimental and Theoretical Increases in Weight**

(Original dry weight of samples 212·1 mg.)
(5 g. Ni = 240 g. $NH_3$ per litre at 20°C, and 100 : 1 liquor ratio)

| Recorded Weight Increase (mg.) | Nickel Content (mg.) | Non-nickel Increase (mg.)— Based on Original Wt. | Based on Final Wt.* | Theoretical Value |
|---|---|---|---|---|
| 23·7 | 17·3 | 6·4 | 5·1 | 5·6 |
| 29·9 | 22·8 | 7·1 | 5·6 | 6·7 |
| 54·2 | 38·3 | 15·9 | 13·5 | 11·2 |
| 54·3 | 38·8 | 15·5 | 14·8 | 11·4 |

* After removal of nickel.

In all cases it is evident that the increase in weight cannot be explained solely in terms of nickel uptake. It is likely, therefore, that other radicals are associated with the nickel atoms incorporated in the wool. These radicals may be hydroxyl, water, or even oxygen, but not ammonia, since there is no recorded increase in the nitrogen content. The weight increase in excess of the nickel content is of the same order as that which would be expected if one extraneous OH, $H_2O$, or O radical were introduced along with each nickel atom, but the agreement is not as close as is desirable. This may be due to nickel being taken up in various forms, some metal being incorporated along with two radicals and some with one. This is a likely possibility in view of the large number of possible sites in the wool molecule.

## General Conclusions

It is evident from the experimental work described in this paper that many factors, including concentration, time, and temperature, affect the adsorption by wool of nickel from solutions of nickelammonium hydroxide. The following more important facts also emerge—

(1) The maximum amount of nickel combined with the wool is about 22%.

(2) The total increase in weight following treatment of wool with nickelammonium hydroxide is greater than that which would be expected from union with nickel atoms alone.

(3) There is no increase in the nitrogen content of the wool following treatment with nickelammonium hydroxide.

(4) Modification of the disulphide or the salt linkings does not affect the total amount of metal finally taken up.

(5) Acetylation reduces the adsorption of nickel.

In view of (4) and of the large amount of nickel adsorbed, it is likely that the union between the nickel and the wool is concerned mainly with groups in the main chains. As a working hypothesis, it is suggested that the nickelammonium hydroxide first causes the wool to swell, thereby facilitating co-ordination with the protein. In support of this, it is found that nickelammonium sulphate, which does not promote great swelling, reacts only very slowly with the fibre. The union between the nickel and the fibre is probably a type of co-ordination, the nickel first co-ordinating as a complex containing ammonia, which is then hydrolysed during rinsing in water.

It is not possible at this stage to explain the mode of combination precisely, partly because the composition of the nickelammonium hydroxide is not known exactly. Dawson and McRae [13] assumed that the co-ordination number of nickel in ammoniacal solution was 4, a view confirmed by application of the conductivity method of Bonsdorff [14]. Following a study of metal ammine formation in aqueous solutions, however, Bjerrum [15] concluded that co-ordination proceeds by steps according to the concentration of free ammonia; co-ordination numbers for nickel ranged from 1 to 6. Although this work was concerned with metal ammine salts, it is reasonable to assume that varying co-ordination numbers will be found in the corresponding bases. It is interesting to record that ethylenediaminonickel hydroxide has the formula $[Ni en_3](OH)_2$ [16], i.e. in this compound the co-ordination number is 6.

It is assumed that when the nickel complex reacts with the wool there is interchange between the co-ordinated $NH_3$ groups and the >NH in the main chains. The amount of nitrogen in the wool used in these experiments is 16·0%. Of this 10·8% is contributed by nitrogen in the main chains and the rest by ammonia, salt links, lysine, arginine, tryptophan, and histidine [17]. Links of the type—

$$\begin{array}{ccc} | & & | \\ HN & \rightarrow Ni \leftarrow & NH \\ | & & | \end{array}$$

would permit 22·4% of nickel to be taken up. This agrees well with the observed amount. In presence of ammonia some $NH_3$ groups will also be co-ordinated with the nickel, and these will be changed on washing to OH or $H_2O$, thus accounting for the total increase in weight. The co-ordination number of the nickel is, however, low, and it would be expected that the nickel-containing protein

would show some evidence of affinity for molecules such as water. This is in fact the case, for the nickel-containing protein has a considerably larger regain than that of untreated wool. This aspect of the work will be discussed in another paper.

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[16] Traube, W., and Lowe, B., *Ber.*, **47**, 1908 (1914).
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## A Note on the Action of Nickelammonium Hydroxide on Proteins in General

J. W. BELL and C. S. WHEWELL

Nickelammonium hydroxide combines not only with wool, but also with feather keratin, hide powder, egg albumen, casein, and formalised casein. Some proteins dissolve yielding red solutions, from which metal-containing complexes may be obtained by addition of ethyl alcohol. The nickel content of these complexes is high. Polyglycine is soluble in concentrated solutions of nickelammonium hydroxide.

During the experiments described in the previous paper it was noticed that when samples of wool were immersed in moderately concentrated nickel-ammonium hydroxide solution (5–10 g. of nickel per litre) for long periods, the wool became excessively degraded and a red coloration appeared in the bottom of the reaction vessel. Since adsorption of nickel by wool is accompanied by the development of a reddish-brown colour, it seems reasonable to suppose that this red solution contains a complex of nickel and dissolved protein.

Experiments were carried out in which wool and hair were treated for long periods (up to several days) at room temperature in nickelammonium hydroxide solutions of various strengths. It was found possible to dissolve large amounts of protein material, the remainder being converted to a gelatinous mass which could usually be lifted out of the solution. The clear red liquor had a high tinctorial value, as a small amount, when added to a separate solution of nickelammonium hydroxide, completely masked the blue colour.

Other proteins also react with nickelammonium hydroxide, turning brown as nickel is adsorbed. Feather keratin passes into solution more rapidly than wool and leaves a comparatively small gelatinous residue; silk dissolves at once even in dilute solutions—so rapidly, in fact, that it is impossible to measure any accompanying dimensional changes. Hide powder dissolves comparatively quickly, leaving a small insoluble residue. Casein and Ardil fibres do not dissolve, though nickel is adsorbed; this resistance may be due to the presence of formaldehyde cross-links. Casein powder and gelatin react rapidly and soon pass into solution. When a solution of gelatin is added to a solution of nickelammonium hydroxide the red colour appears at once. Raw egg albumen likewise reacts very rapidly, but the reaction is retarded if the albumin is first coagulated by heating. In collaboration with Dr. A. B. Meggy, a most important result was obtained with the synthetic polymer polyglycine, for it was shown that when this substance is treated with concentrated nickel-ammonium hydroxide (preferably stronger than 10 g. of nickel per litre) it dissolves slowly to yield a deep red solution, although there is no adsorption of nickel by the undissolved polymer. This is of interest in view of the scarcity of solvents for polyglycine.

These red solutions are decomposed by adding dilute sulphuric acid, and the nickel-protein complexes can be isolated by diluting the solutions with ethyl alcohol. From keratin and polyglycine complex solutions a gummy brown precipitate is produced which rapidly coagulates, but the precipitates obtained from complexes of nickel and hide powder, silk, gelatin, and albumen are of a gluey consistency and are hardened only after repeated macerations in alcohol. A series of light brown and dark brown powders was obtained, variations in shade being due, presumably, either to variations in the state of subdivision of the powder or to admixture of coprecipitated nickel hydroxide or unchanged protein. Owing to the possible impurity of the powders, too much significance cannot be placed on analytical results, but the nickel content is high and of the same order as that found for nickel-containing wool.

DEPARTMENT OF TEXTILE INDUSTRIES
THE UNIVERSITY
LEEDS

(*Received 19th March 1952*)

# Notes

## Proceedings of the Council

At a meeting of the Council held at the Offices of the Society, 19 Piccadilly, Bradford, on 18th June 1952, the proceedings included the following items of interest:—

INTERNATIONAL FEDERATION OF ASSOCIATIONS OF TEXTILE CHEMISTS AND COLOURISTS—After careful consideration of an invitation to join the Federation, it was decided to take no action for the present.

TERMS AND DEFINITIONS COMMITTEE—It was resolved to invite Mr. C. O. Clark and Mr. J. S. Ward to serve on this Committee.

MEMBERSHIP COMMITTEE—It was agreed that the Manchester Section should be represented on this Committee by Mr. C. P. Tattersfield.

MEMBERSHIP—Six applications for ordinary membership were approved.

## Meetings of Council and Committees July

Council—23rd
Finance—23rd
Publications—15th
*Colour Index* Editorial Panel—24th
Fastness Tests Co-ordinating—30th
Diploma—23rd

## Tentative Definitions

The Terms and Definitions Committee will welcome comments on the following tentative definitions:—

18. MIGRATION

The movement of dye from one part of a dyed material to another.

19. LEVELLING

Migration leading to uniform distribution of dye in a dyed material.

20. STRIKE

The initial rate of dyeing. It may be measured by the slope of the exhaustion time curve at the origin.

21. CRABBING

A treatment given to fabrics composed wholly or partly of wool with the object of improving dimensional stability in subsequent wet processing at temperatures not exceeding those obtaining during the treatment, which consists in immersing the fabric in a hot or boiling aqueous medium whilst under tension, and cooling whilst still held in the desired position.

22. SKITTERINESS

An undesired speckled effect in a yarn or fabric arising from differences in colour or in depth of dyeing between adjacent fibres or portions of the same fibre.

## Second Continental European Fastness Meeting

Following the first meeting held in Basle on 23rd–24th February 1951, a second meeting was organised by the French, German, and Swiss Fastness Committees in Paris on 25–26th April 1952. The main outcome of the Paris meeting was the formation of a permanent organisation, to be known as E.C.E. (Groupement d'Études Continental Européen pour la Solidité des Teintures et Impressions, Vereinigung Europäisch-Continentaler Echtheitskommissionen) under the chairmanship of Dr. J. Weibel (Switzerland), which the principal industrial countries of the Continent have joined. Dr. P. W. Cunliffe and Mr. K. McLaren (Chairman and Honorary Secretary respectively of the Fastness Tests Co-ordinating Committee) attended as observers on behalf of the Society, and the former outlined the Society's work during the past year directed towards securing international agreement on fastness testing through the I.S.O., making special reference to the grey scale. It was agreed that every effort should be made to reach agreement at the I.S.O. meeting to be held in the U.S.A. in November 1952 (cf. J.S.D.C., **67**, 307–308 (Aug. 1951)).

## Fédération Internationale des Associations des Chimistes du Textile et de la Couleur

Steps were taken for the reconstitution of the Federation at a meeting held in Basle on 29th March 1952, attended by delegates from Austria, France, Germany, Holland, Italy, and Switzerland. Mr. J. G. Grundy attended as an observer on behalf of the Society. A revised set of bye-laws was approved for submission to the Councils of the societies represented at the meeting. It was decided not to publish a separate journal, as was the case before the Second World War. Dr. R. Haller agreed to act as president, Dr. H. Ris as honorary secretary, and Herr P. Deck as honorary treasurer.

The Federation was founded in Milan in 1930 by Dr. G. Tagliani, its first president. International congresses were held in Paris in 1931 and in Stuttgart in 1936. It is proposed to hold the third in Basle in September 1953.

## International Dyeing Association

An "Association Internationale de la Teinture Textile" has been established in Paris. Its objects include the promotion of personal contacts among member associations, the exchange of experience, and the safeguarding of the interests of the industry at the international level. Employers' organisations in the following countries have so far joined—Austria, Belgium, France, Germany, Italy, the Netherlands, and Switzerland. Paris has been chosen as headquarters of the new association for the first two years, and M. Pierre Baumgartner (Ste. Marie-aux-Mines, Alsace) has been elected its first president.

## British Science Centre

Lord Woolton stated in the House of Lords on 12th June 1952 that a site down-river from Waterloo Bridge and facing Somerset House had been reserved by the London County Council, the planning authority.

### Higher Technological Education

Lord Woolton stated in the House of Lords on 12th June 1952 that the Government is convinced that the improvement of facilities for higher technological education is a most important means of increasing productivity in industry, and that this can best be done by having at least one institution of university rank devoted predominantly to the teaching and study of the various forms of technology. The Government recognises the important contributions which technical colleges can make to higher technological education, and details of proposals for making improved financial assistance available for selected colleges and courses will be announced shortly by the Ministry of Education. The Government does not propose, however, to establish a non-teaching award-making body under the title of "Royal College of Technology".

### Textile Institute Conference 1953

This will be held at Llandudno, North Wales, during Whit week, 25–30th May 1953, on the design and testing for special purposes of fibres, yarns, and fabrics.

### Chemical Abstracting in English

Attempts to avoid duplication of chemical abstracting services in English have again failed. Relevant correspondence between the American Chemical Society and the (British) Bureau of Abstracts is published in the issue of *Chemistry and Industry* for 21st June 1952 (pp. 556–557).

### Schweizerische Vereinigung der Färbereifachleute

The S.V.F. celebrated its ten years of existence on 21st and 22nd March 1952 in Basle. The President, Herr Holderegger, opened the technical meeting on the Saturday, and honorary membership was conferred on Herr O. Landolt, a founder member.

### Woad

At the Royal Society Conversazione held on 22nd May 1952 the Science Museum displayed an oil painting of the last movable woad mill. Woad making persisted as late as 1932 in Lincolnshire.

### Indanthren Trade Mark Association

An association, with headquarters in Frankfurt-am-Main, has been founded to ensure uniform policy in the use of the name *Indanthren*, and has formed three committees—technical, legal, and publicity. The members are the dyemaking firms Basf, CFM, FBy, and FH (including NCO), the Gesamtverband der Deutschen Textilveredlungsindustrie e.V., the Vereinigung der Stoffdruckereien e.V., and the "Indanthren"-Textil-Einkaufsgemeinschaft G.m.b.H.

### Production of Dyes in 1951 in the U.S.A.

The U.S. Tariff Commission reports that the production of dyes in the U.S.A. in 1951 was (all weights in million lb.) 186, i.e. 5% less than in 1950. Sales of dyes in 1951 were 159 worth $174 million, a decrease of 15% in weight and 9% in value on the 1950 figures. Of the 1951 production azo dyes accounted for 36%, anthraquinone vat dyes 22%, indigoid and thioindigoid 13%, and sulphur dyes 12%. The only group which showed increase in production and sales compared with 1950 was the anthraquinone vat, where production was up by 16% and sales by 7%. Production of indigoid and thioindigoid dyes was 26% less in 1951 than in 1950. Classified by usage, vat dyes were 37% of all dyes produced, direct dyes 20%, sulphur dyes 12%, and acid dyes 10%, but production and sales of all four classes were less than in 1950. Production of azoic dyes and their components was 7·1, a decrease of 16%, sales being down by 20%. Production of indigo was 20·5 compared with 26·2 in 1950, sulphur black 11·2 against 13·5, Direct Black EW (*C.I.* 581) 7·1 against 8·2, jade green (*C.I.* 1101) 5·7 against 6·4, and Indanthrene Khaki 2G 4·8 against 1·3 million lb.

C O C

### French Output of Dyes

The monthly average increased from 1271 tons in 1950 to 1437 tons in 1951.

### Brazil now Self-sufficient in Certain Dyes

The Cartiera do Exportação e Importação, Cexim, the executive agency of the Bank of Brazil, announces that no more licences will be granted for the import into Brazil of the following dyes—*Colour Index* Nos. 138, 151, 331, 332, 370, 401, 406, 420, 448, 502, 520, 581, 582, 593, 594, and 596—as Brazilian production is now sufficient to meet home demands.

C O C

### Phthalic Anhydride in Holland

The manufacture of phthalic anhydride in Holland is under joint development by the A.K.U. and the Dutch State Mines, and it is hoped that there will be a considerable export surplus.

### Health Hazards of Naphthylamines

In reply to a question by Mr. H. Boardman in the House of Commons on 6th May 1952, the Minister of Labour stated that there was reason to believe that the manufacture of $\alpha$- and $\beta$-naphthylamine is associated with the occurrence of cancer of the bladder among the workers concerned. This disease occurs also among the general population, but the extent of the risk attributable to the manufacture and use of these substances is not fully established.

### Sulphuric Acid Consumption

The consumption of sulphuric acid in the United Kingdom for various trade uses during the first quarter of 1952 was (in tons of 100% $H_2SO_4$)—dyes and intermediates 19,529, rayon and transparent paper 57,403, textile uses, 4698. The total consumption works out at 438,819.

### Mishap due to Aniline Fumes

While removing a concrete lining from a tank which had contained some aniline oil, two men were overcome by fumes, at Stanningley, near Leeds, on 8th May 1952. It was stated that the tank had not been used for five years, and had been recently washed out with caustic soda and then steamed.

### Evaluation of Textile Printing Pastes

According to the Annual Report for 1950–51 of the D.S.I.R., the British Cotton Industry Research Association is undertaking fundamental research into the rheological properties of printing pastes, measurements of which at only two different rates of shear are of great assistance in evaluating the pastes.

### The B.S.I. "Kite" Mark

The B.S.I. "Kite" mark, which has been developed to indicate that the commodity on which it appears complies with certain quality requirements laid down in a British Standard, will now also be used in the fields previously covered by the utility schemes. The use of the mark is controlled by the B.S.I., and a manufacturer may not apply the mark to a commodity unless he has obtained a licence to do so from the B.S.I. Conditions of licence and other information may be obtained, on application in writing, from the British Standards Institution, 24 Victoria Street, London S.W.1.

### Wool Research Institute in Aachen

A Wool Research Council has been set up in Düsseldorf, and will pass on problems for solution to the newly founded Wool Research Institute of the Technische Hochschule in Aachen.

### Superfine Fibres

Work on the filtration of aerosols at the Naval Research Laboratory in Washington, notably by A. van Wente and E. L. Boone, has led to the production of thermoplastic fibres 0·3–2·0 $\mu$ in diameter (*Ind. Eng. Chem.*, **44**, 13A–15A (June 1952)). The hot resin melt is extruded into a high-velocity stream of heated gas, usually air. Extremely strong fabrics, free from pinholes, result from such fibres. Thus 1 lb. of resin, e.g. nylon, will make 400,000 miles of fibre.

### Phrilon

Phrix Gesellschaft m.b.H., Hamburg, have marketed, under the name of *Phrilon*, a new polyamide fibre based on ε-aminocaproic acid. It is stated to have a breaking length of 40–50 km., an extension at break of 35–55%, a wet : dry strength ratio of 90%, a regain at 65% R.H. and 20° C. of 3%, and a m.p. of 213–215° C. A.E.S.

### Movil—an Italian Polyvinyl Chloride Fibre

Movil is a polyvinyl chloride fibre being made in Italy by the Polymer di Terni under licence from the French Rhovyl S.A. Output is to be 3000 kg. a day. C.O.C.

### List of Patents in Force

Copies of the *List of Patents in Force at the end of 1951* are now obtainable from the Sales Branch, Patent Office, 25 Southampton Buildings, Chancery Lane, London W.C.2, at 15s. per copy (including postage).

### English Translations of Russian Journals

The two journals *J. Appl. Chem. U.S.S.R.* and *J. Gen. Chem. U.S.S.R.* are now available in English translation from the Consultants Bureau, 152 West 42nd Street, New York 18, N.Y., at $80.00 and $95.00 respectively per annual volume. Translations of individual papers may be purchased at $5.00 each.

### Transport of Scientific Instruments

Unesco has recommended to its member States measures for the rapid and safe transport of certain scientific instruments by arranging for customs inspection to take place in the laboratory itself in the presence of a competent person. Such arrangements are already in force at the National Physical Laboratory at Teddington, at the National Bureau of Standards in Washington, and at similar national laboratories in Paris, Leningrad, Tokyo, and Germany.

### Professor K. O. H. Meyer 1883-1952

The death of Professor Meyer is reported from Menton[1]. Born in Dorpat (Estonia), in 1907 he obtained his Ph.D. under Hantzsch at Leipzig for a thesis on halochromy. After work on keto-enol tautomerism at Munich, he joined the B.A.S.F., later the I.G., at Ludwigshafen in 1921. Here he became interested in dyeing theory and then in the nature of the substrates, his study of natural substances of high molecular weight, begun in 1927 and continued till his death, leading in 1930 to the first manual on the subject, written in collaboration with H. Mark. In the course of his occupation of the chair of inorganic and organic chemistry at Geneva from 1932, he contributed to the establishment of the structure of both natural and regenerated cellulose, rubber, gutta-percha, and chitin; he distinguished the two substances amylose and amylopectin in starch; and he showed that pure α- and β-amylases from different sources differed greatly in properties although having the same chemical effects.

[1] van der Wyk, A. J., *Helv. Chim. Acta*, **35**, 1418–1422 (June 1952).

# New Books and Publications

## Final Report on the Census of Production for 1945

### Volume 2 Trade B

### Dyes and Dyestuffs

H.M. Stationery Office. Pp. 17. 1952. Price, 1s. 9d.

Twenty-six tables embodying data on firms in Britain wholly or mainly engaged in making intermediates, dyes, and tanning extracts. Data include production and sales, number of firms and their location by districts, materials purchased and fuel consumption, number of employees and remuneration, costs of various services, e.g. advertising, plant maintenance, and research in the case of larger establishments, etc. C. O. CLARK

## Veredler-Jahrbuch Deutscher Färberkalender 1952

Edited by O. Mecheels. Pp. 264 + 64. Munich: Franz Eder Verlag. Price, 82.25.

This Kalender, the largest of the post-war issues, opens with a series of thirty articles of interest to dyers and finishers. In particular, four deal with the natural, as well as with the partly and wholly synthetic, fibres, and include methods of estimation of separate fibres in admixture. Ten articles are concerned with the dyeing of individual and mixed fibres, while others classify the dyes by chemical constitution, dyeing behaviour, and fastness properties. Auxiliary agents and their relation to fibres, as well as the qualitative separation of detergents, etc., are included together with analytical tables.

The usual catalogue of new dyes and auxiliary products appears. This is probably the most important section of the book from the point of view of members of the Society, as it enables dye-users to keep fully *au fait* with the latest developments in both Germany and Switzerland. A useful feature is that when the product replaces those previously manufactured by the I.G. the name of the pre-war product is indicated.

A most useful book to the dye-user who can read German. A. THOMSON

## Silk

### Biology, Chemistry, Technology

By P. Carboni, translated by K. Walter. Pp. xi + 248. London: Chapman & Hall Ltd. 1952. Price, 37s. 6d.

According to the publisher's note, this book is a translation of a standard work in Italy which has been extensively revised by the author for the English edition and to which several sections have been added. An adequate implementation of this claim would possibly have provided a book of unquestionable value to those interested in the science and technology of silk; unfortunately, however, this objective has not been attained, and this is to be regretted in view of the present non-availability of up-to-date textbooks on silk. This book, in fact, well exemplifies the responsibility of the translator of technical and scientific books, who must have not only a thorough knowledge of the basic languages concerned, but also an extensive acquaintance with the science and technology of the relevant subjects, again in both languages. Of these two requirements, the second is perhaps the more important, and it is in this respect that the translation of Carboni's work is very much open to criticism, although, in fairness to the translator, it should be added that there are errors, lack of clarity, etc. that are doubtlessly present in the original version.

The first four chapters deal with the chemical, physical, and biological characteristics of the cocoon, sericultural methods (with special emphasis on Italian practice), the chemical structure of silk fibroin, characteristics of raw silk threads, and the methods of silk reeling. The information given will be useful to those interested in sericulture, but the discussion of the structure of fibroin is inaccurate and not up-to-date. In the brief description of the chemistry of fibroin, reference is made merely to the work of Fischer and Abderhalden: dipeptides are generally misspelt, and glycyl-D-alanine is considered to be identical with methyldiketopiperazine. X-Ray investigations of fibroin are inadequately considered (the attempted theoretical treatment could be omitted with advantage) and the appended photographic reproduction of "An X-Ray of Silk" merely resembles a photograph of a total eclipse of the sun. In a discussion of the specific gravity of silk, the more recent work of Heertjes (*Rec. Trav. chim.*, **60**, 329 (1941); **61**, 751 (1942)) has been disregarded. The process of reeling is described fully and authoritatively. Several pages are devoted to the hardness of water, and it is proposed that hardness should be expressed in "millivals (mval.)" where 1 mval. is 1/1000 of the equivalent weight of CaO or $CaCO_3$ (which, according to the author, is 0·28 mg. of CaO or 0·50 mg. of $CaCO_3$; presumably 1/100,000 of the equivalent weight is intended).

Chapter V is a fairly comprehensive account of the methods of testing raw silk, although here again the Italian methods are emphasised. The impossible has been attempted in the reproduction of the photographic standards of cleanness. In the treatment of regain, no reference is made to hysteresis or the difference between adsorption and desorption isotherms. The suggestion (p. 152) that silk degumming can be satisfactorily achieved by dilute caustic alkali is very much open to question.

Chapter VI, on the throwing of silk, is badly written and in places (e.g. the explanation of loss of lustre with twist) erroneous.

Chapter VII is headed "Silk Dyeing Processes", but deals mainly with vegetable and tin weighting. About four pages are devoted to dyeing, and give far less information than is obtainable from any dye manufacturer's manual.

Chapter VIII is a reasonably comprehensive and accurate account of the spun-silk industry, although no mention is made of the cap-spinning frame, only of the "ring-spindle" frame.

The book concludes with Chapter IX, giving commonly accepted methods for the analysis of weighted silks and also of fabrics of mixtures of silk with other fibres.

Scientifically, this book is unsatisfactory. Apart from the frequent use of terms such as "glycocoll" for glycine, "sericteries" for silk-glands, "7 per mille soap" for 0·7% soap solution, etc., there is much evidence of careless and erroneous expression. Thus alcohol and "benzol" are described as ether solvents; in the determination of water-soluble material in cocoons, the material is stated (p. 20) to be "first weighed at 120° C.", and on p. 21 it is suggested that acetic acid is formed from ethanol during normal Soxhlet extraction. The reader will learn many Italian words for processes and materials—and also some incorrect English translations: a few examples from the many present are that slubs in the seriplane test are called "ruffling", a word also used for chafing, whilst silk soaking is referred to as "sizing". The bibliography is meagre, the subject index is of minimum length, and the text does not demand an author index.

This book, on the biology, chemistry, and technology of silk, cannot be recommended with unqualified confidence to the biologist, chemist, or technologist; nor to those students who can afford its price, which is unduly high for a book of this kind.

F. O. HOWITT

## Thiophen and its Derivatives

By H. D. Hartough. Pp. xvii + 533. New York and London: Interscience Publishers. 1952. Price: $16·50.

In the third volume of this new series of monographs Dr. Hartough aims "to cover critically all phases of thiophen chemistry and to point out some of the existing problems yet to be solved". The result of his efforts is a book nearly twice the size of *Die Chemie des Thiophens* (Steinkopf), published eleven years ago.

In developing his subject, Dr. Hartough has kept to the general plan of Steinkopf's treatise, opening with a discussion of the history of the subject, of the system of nomenclature used, and of the physical properties of thiophen compounds. There follows a chapter (by F. F. Blicke) on the biological and pharmacological properties of thiophen and its derivatives in which an account is given of three antihistaminic drugs which have found clinical application and which represent the sole commercial use for thiophen compounds so far discovered. The rest of the book is concerned with the synthesis and properties of thiophen and its derivatives—alkylthiophens, halogenothiophens, nitro and amino compounds, carboxylic acids, and the like, a separate chapter being devoted to each main class of compound. A rather unusual feature for a work of this kind is the appendix, in which laboratory preparations of a considerable number of thiophen compounds are described. These are mostly of the type likely to be useful to a chemist beginning research in this field, who would find the spectroscopic data given in Chapter IV also very helpful. The book is well documented, and many tables of physical constants (with literature references) are given. One of these (p. 238), in which are listed several azo compounds of the thiophen series, displays a rather glaring error in its heading, "Diazo Derivatives of Thiophen".

When discussing the theoretical aspects of his subject, Dr. Hartough adopts a somewhat uncompromising attitude towards those pioneers of thiophen chemistry who stressed the similarity between the newly discovered compound and benzene. He considers that statements in textbooks of organic chemistry such as—"Thiophen chemistry is quite similar to benzene chemistry. Thiophen is perhaps more reactive . . . . . " have hindered thiophen research and blames Victor Meyer for their origin. Now, although recent research may have revealed facts which, if known to Victor Meyer, would have led to some modification of his views, it seems absurd to assert that: "the chemistry of thiophen and benzene are to be compared about as closely as a zoologist would compare the tortoise and the boa constrictor", and one receives the impression that in adopting such an extreme attitude, Dr. Hartough is trying to grind an axe in the interest of his chosen subject. For the chemistry of thiophen is on the whole dull, and possesses few of the features which go to make furan, its oxygen analogue, interesting; e.g. thiophen does not show diene-like behaviour towards dienophiles, nor is the ring readily opened with the production of useful aliphatic compounds. Technical interest is at present lacking (except for the three drugs mentioned) and there appears to be little promise in the immediate future. One wonders whether, for most readers, the subject is not already dealt with adequately in the several shorter reviews which have recently appeared elsewhere.

W. F. BEECH

## New and Revised British Standards

The following new or revised British Standards have recently been published, and are available post-free from the Sales Department, 24 Victoria Street, London S.W.1.

*B.S.* 767 : 1951

HYDROEXTRACTORS AND CENTRIFUGAL MACHINES

This revised standard covers machines, running at 400–3000 r.p.m., for use in laundries and the textile and other trades. The standard covers details of basket construction, quality of materials, safety designs, tests, and marking. Appendixes give information on operation and maintenance. Price, 2s. 6d.

*B.S.* 1118 : 1952

SHRINKAGE ON LAUNDERING OF WOVEN COTTON AND LINEN FABRICS

This revised standard specifies more closely the procedure to be adopted for the centrifuging and ironing of specimens undergoing test. It includes sections dealing with dimensions, preparation and marking of test specimens, method of conducting and completing the washing test, and the method of recording the results of tests. Appendixes refer to methods of marking specimens, suitable compositions of washing solutions, methods of removing surplus water, and statistical notes on data

obtained in the main series of tests upon which the revision has been based. Price, 2s. 0d.

*B.S.* 1681 : 1951

WOOL BLANKETS FOR HOSPITAL AND LOCAL AUTHORITY USE

This standard has the purpose of co-ordinating the requirements of users in this particular field. It thus enables users to purchase to a well defined quality and it will also assist in the production of blankets by enabling manufacturers to concentrate upon a recognised range of standard constructions and sizes. The schedule of standard finished requirements gives the reference number, description, sizes and tolerances, weight per blanket, weave, colour, threads per inch, and minimum breaking loads. The text deals with the composition, tolerance on construction, provision for marking, range of standard colours and degree of colour fastness, and bleaching and raising requirements. Provision for whipping and side-stitching is also included. Shrinkage requirements are laid down both for relaxation and for laundering. Procedures for sampling and conditioning, and for testing the specification particulars are given. Details are given of standard sealed blankets held by the B.S.I. for reference purposes, and of standard samples which may be purchased for purposes of testing. Price, 2s. 6d.

The book of standard samples (*B.S.* 1681 P : 1951) includes a range of seventeen samples for purposes of testing colour fastness to light and washing and for purposes of general comparison in respect of shade of colour, degree of bleaching, appearance, raising, handle (or feel), and other properties not specifically defined in *B.S.* 1681. Each sample is 12 in. × 4 in. in size and the range is representative of all the blankets dealt with in the main specification. Price, 25s. 0d.

The shrinkage-testing samples (*B.S.* 1681 P/S 1–5), intended for purposes of testing to determine relaxation shrinkage and shrinkage on laundering (felting shrinkage), each measure 24 in. × 24 in., and the range is representative of all the blankets dealt with in the main specification. Price, 12s. 6d. each.

*B.S.* 1781 : 1951

LINEN TEXTILES FOR USE BY HOSPITALS AND LOCAL AUTHORITIES

This new standard includes a complete range of linen bedspreads, pillow cases (slips), towels (including kitchen cloths), and sheets of particular application for hospital and institutional use. The specification clauses deal with materials, manufacture, identification marking, and testing. A series of four tables gives technical particulars, and eight appendixes are included dealing with methods of test. Price, 2s. 6d.

Standard sealed samples of made-up articles which are representative of the full range are being held for inspection at the offices of the B.S.I. In addition, standard pattern books (*B.S.* 1781 P) containing twenty-one cuttings, each 6 in. × 4 in. in size, which are fully representative of the materials specified, may be obtained as a guide to type and quality and for general comparison in checking appearance, degree of bleaching, finish, handle (feel), and other properties not defined. Price, 20s. 0d.

*B.S.* 1797 : 1952

TABLES FOR USE IN THE CALIBRATION OF VOLUMETRIC GLASSWARE

This standard contains two sets of tables, relating to vessels made of soda glass and borosilicate glass respectively. Each set of tables is appropriate to the conversion of the observed weight, in grams, in air of average density, of the distilled water contained or delivered by a glass vessel at a known temperature, into the volume of the vessel at 20°c. In addition, tables are provided for the correction for the departure of the effective air density from the average, the conversion of the weight in air of the mercury contained or delivered by a glass vessel at a known temperature to the volume of the vessel at 20°c., and the conversion of the nominal volume of a glass vessel at 20°c. to the weight in air of the mercury contained in or delivered by it at various temperatures. The tables allow for the correct density of the liquid, the change of volume of the vessel with temperature, and the buoyancy of the air during the weighing. Price, 10s. 6d.

# Abstracts from British and Foreign Journals and Patents

*(The titles of abstracts may be modified. Abbreviations of names of firms are listed in* J.S.D.C., **68**, *23 (Jan. 1952); while other abbreviations and symbols, together with a list of the periodicals abstracted, will be found at the end of the annual index.)*

## I—PLANT; MACHINERY; BUILDINGS

**Jigger used for Processing in Open Width.** C. Villeneuve. *Industrie text.*, **66**, 225–226 (July 1949): *J. Textile Inst.*, **43**, A 312 (May 1952).

A new kind of jigger, which can be used in desizing, bleaching, scouring, and dyeing baths, is described. On this jigger the width of the material is held under tension over the small paddles of the machine. As it passes over the paddles the material is pleated at a sharp angle. This ensures that air bubbles are removed from the fibres and do not prevent close contact with the liquid. Liquid is squeezed out by the tension and fresh liquid replaces it, thus accelerating the action. The pleating at a sharp angle opens up the spaces between the threads and helps the liquid to penetrate. C. J. W. H.

PATENTS

**Spindles for Package-dyeing Machines.** E. A. Stienen. *BP* 671,557

An improved form of spindle, which allows a greater volume of dye liquor to pass through it, thus enabling more packages to be dyed per spindle, is described. C. O. C.

**Warp Drying.** E. M. Holt. *USP* 2,583,427

A warp drier in which the splitting rolls tend neither to become sticky nor to collect lint. C. O. C.

**Fabric-conveying Apparatus.** DuP. *USP* 2,579,563

Mechanism for forwarding and piling fabric, e.g. in a J-box, without imparting undesirable tension or stress. C. O. C.

**Dye Jigs.** Sir James Farmer Norton & Co.
*BP* 671,437

In a jig whose rollers are each driven by a D.C. motor, starting and stopping of the motors are controlled so that the cloth is not jerked on starting up and does not slacken between the rollers when the take-on roller stops. C. O. C.

**Winch.** Leumetals. *BP* 671,969

A winch, on which the fabric does not slip, is built up of a number of curved plates, each of which comprises a series of flat longitudinal surfaces corresponding with the flat faces of a normal winch. Each pair of flat surfaces is separated by a curved longitudinal recess extending the whole length of the winch, and each flat surface has one or more rows of radial holes in it.

*BP* 671,970

A main winch of circular cross section is accompanied by a secondary winch of oval cross section. The main winch drives the fabric without causing any alteration in the tension in it, while the elliptical winch takes no part in the driving of the fabric but acts solely to fold it in the back. C. O. C.

**Stopping the Travel of an Endless Rope of Fabric for Inspection at a Predetermined Place in the Rope.** United Piece Dye Works. *BP* 673,403

**Speed Control for Rollers.** F. Smith & Co. (Whitworth). *BP* 673,000

The speed of rollers in machines where fabric passes continuously between successive pairs of rollers is controlled to allow for shrinkage or extension in the fabric. C. O. C.

**Tenter.** Celanese Corpn. of America. *USP* 2,577,880

Feeding the cloth to the tenter chains at a linear speed greater than the speed of the chains introduces sufficient slack into the cloth to allow it to shrink during drying, and so results in a cloth having dimensional stability. C. O. C.

**Rapid Changing of Calender Rolls.** P. Dornbusch. *BP* 672,920

Transmission gearing for coupling and driving calender rolls is so devised that the rolls can be rapidly changed, without any necessity for the gear wheels to be removed from the old rolls and fitted on the new rolls. The same gears can be retained on the calender even when the replacement rolls differ in diameter from those they are replacing. The working of the gears is unaffected by variations in the thickness of the material being calendered. C. O. C.

**Winding Continuous Webs.** La Cellophane. *BP* 673,169

Apparatus for winding continuous lengths of regenerated cellulose sheeting or similar webs on to rollers while maintaining constant lengthwise tension in the wound material. C. O. C.

**Web Register Control System for Multicolour Printing.** Askania Regulator Co. *USP* 2,583,580

**Driving Mechanism for moving Fabrics across Inspection Tables.** Celanese Corpn. of America. *USP* 2,583,674

**Paddles for Garment-dyeing Machines.** Longclose Engineering Co. *BP* 673,192

A welded paddle can be made without distorting the end plates if these are dished, preferably so that they are closer to each other in the region of their axis than at their peripheries. C. O. C.

**Tumbler-type Clothes Drier.** Lovell Manufacturing Co. *USP* 2,583,850

**Hat Bat Shrinking Machine.** United States Hat Machinery Corpn. *USP* 2,579,814

**Drum Washing Machine having Improved Liquor Circulation.** Isaac Braithwaite & Son Engineers. *BP* 673,887

**Laundering.** E. Sulzmann. *BP* 672,755

Several washing machines are arranged in a ring and connected in series, so that the liquor, which flows always in the same direction, is uninterruptedly supplied to and removed from each machine. Each machine can be uncoupled from the ring to enable it to be discharged or cleaned and recharged with dirty articles, its place being taken by another machine along the ring. The liquor thus passes through several machines, and is finally used for the first washing in a machine which has just been charged with dirty articles. This enables the rinsing and washing liquors to be used up without a residue. C. O. C.

**Automatic Control of Washing Machines.** Gebrüder Poensgen. *BP* 673,292

A sequence regulator with measuring device for independent regulation of the quantity of water, temperature, and detergent solution for each complete series of washing processes on each batch of goods from the first soak to the final rinse. C. O. C.

**Spotting Machines.** Bill Glover. *BP* 672,442

A hollow spotting table with a foraminous cover is movably mounted. Suction means connected with the table are controlled by moving the table relatively to its support so as to cause a downdraught of air through the cover and the interior of the table. C. O. C.

**Combined Tumble-action Washer and Squeezer Extractor.** Avco Manufacturing Corpn. *BP* 671,631

A combined washer and extractor uses a flexible container as a tumble action washer and as a suction-collapsed flexible-wall extractor. C. O. C.

**Screen Printing Machine.** L. R. Wade. *USP* 2,581,775

A screen printing machine, completely automatic except for insertion and removal of the work, has a squeegee-operating mechanism with a readily adjustable stroke, so that screens of different areas may be interchanged. The screen is raised and lowered in timed relation to the movement of the squeegee, the return movement of the latter occurring while the screen is raised, so that during such time the work may be changed. The screen, carrier, and squeegee-operating mechanism share a common pivotal axis, so that tilting the carriage does not affect the working of the squeegee operating mechanism. C. O. C.

**Intaglio Printing of Regenerated Cellulose or other Non-fibrous Films.** La Cellophane. *BP* 672,836

Means for drying the printed material in continuous intaglio printing. C. O. C.

**Electrostatic Printing.** W. J. Hooper and W. C. Huebner. *USP* 2,583,375

Apparatus is described whereby the ink is transferred electrostatically from the printing roller to the material to be printed. C. O. C.

**Garment Pressing and Folding.** W. O. Kramer. *BP* 673,568

**Flame Gun for Spraying Powdered Materials.** G. Bourdillon. *BP* 671,864

**Spraying Booth.** Benjamin Electric Manufacturing Co. *USP* 2,583,489

**Coating Paper.** Minnesota & Ontario Paper Co. *USP* 2,582,407

Apparatus which coats one or both sides of paper having wide variations in moisture content is described. C. O. C.

**Emulsifying Machine.** H. E. Zehnder. *BP* 673,409

## II—WATER AND EFFLUENTS

PATENT

**Automatic Regeneration Device in Ion-exchange Plants.** John Thompson-Kennicott. *BP* 672,754

An ion-exchange process includes a cation and an anion unit to be successively traversed by the water being treated, and is fitted with an auxiliary anion unit through which a small proportion of the water is passed. An electrical device gives a visual or audible signal when the conductivity exceeds a certain value; further devices can be fitted to ensure either automatic regeneration or plant shut-down. J. W. B.

## III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

**Infrared Absorption Spectra of Aluminium Soaps.** W. H. Harple, S. E. Wiberley, and W. H. Bauer. *Anal. Chem.*, **24**, 635–638 (April 1952).

Infrared absorption spectra furnish evidence that the mono- and di-soaps of aluminium with various fatty acids are definite chemical compounds, probably of covalent structure. Absorption bands corresponding to free fatty acid are present only when the proportion of fatty acid is in excess of that which corresponds to a disoap, and this excess may be quantitatively removed by extraction with


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for emulsifying
free rinsing
for wetting out
unaffected by hard water
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for all types of fabric
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isooctane at 0·5° C. The "trisoap" does not therefore exist as a definite chemical compound. There is also evidence that the hydroxyl groups are bonded in the monosoaps, but are free in the disoaps; both free and bonded groups are present in soaps of intermediate composition.
J. W. D.

**Phthalocyanine Lubricating Greases.** V. G. Fitzsimmons, R. L. Merker, and C. R. Singleterry. *Ind. Eng. Chem.*, **44**, 556–563 (March 1952).

Phthalocyanine pigments are effective gelling agents for the preparation of greases from petroleum oils, silicones, aliphatic diesters, polyalkylene glycol ethers, and fluorocarbons. These greases contain ca. 80% liquid by vol., and are suitable for use at much higher temp. than conventional soap greases. They maintain their structure to above 300° C. and for extended periods at 200° C. They are water-resistant, shear-stable, and less susceptible to oxidation than the corresponding soap greases. At high temp. they tend to stiffen rather than soften. The phthalocyanine pigment is not abrasive. Special alloy steels are necessary in bearings operating at > 200° C.
W. K. R.

**Solutions of Metal Soaps in Organic Solvents. III—Aggregation of Metal Soaps in Toluene, *iso*Butyl Alcohol, and Pyridine.** S. M. Nelson and R. C. Pink. *J.C.S.*, 1744–1750 (May 1952).

The ebullioscopic method has been used for estimating the degree of aggregation of a number of metal soaps in various solvents. In toluene, it is strongly dependent on the length of the hydrocarbon chain and on the polarity of the soap; the more polar soaps form larger micelles or are insoluble, while increase of chain length in soaps of the same metal leads to a decrease in the degree of aggregation. In the polar solvents isobutyl alcohol and pyridine, the associating effect of the soap dipoles is reduced, and unimolecular solutions are obtained at low concentrations. Stability of the soap micelles is due to dipole interaction and to the decrease in interfacial energy on aggregation.
H. H. H.

**Sodium Salts of Pectin and of Carboxymethyl Cellulose in Aqueous Sodium Chloride. I—Viscosities. II—Osmotic Pressures.** D. T. F. Pals and J. J. Hermans. *Rec. Trav. chim.*, **71**, 433–457 (I) and 458–467 (II) (April 1952).

**I**—The measurement of the intrinsic viscosities of polyelectrolytes in dilute salt solution by extrapolation of the $\eta/c$ versus $c$ curves is difficult because they show a maximum where the equivalent concentration of the polyelectrolyte is of the same order of magnitude as the salt concn. A more reliable result is obtained if the total effective ionic strength is kept constant, when the above plot becomes linear. The intrinsic viscosities of a pectinate and three samples of sodium carboxymethyl cellulose have been examined in aqueous sodium chloride solutions, and their behaviour is explained satisfactorily by the theory of Hermans and Overbeek. In the high precision aimed at, the effect of surface tension becomes of importance. A study of this was made, and on this basis an Ubbelohde viscometer was preferred to an Ostwald viscometer.

**II**—The osmotic pressures of the materials examined above were measured in salt solution using a Fuoss and Mead osmometer in order to measure their molecular weights. The measurements made were found to be in reasonable agreement with the Donnan equilibrium for membranes, and the mol. wt. were $4{\cdot}6 \times 10^4$ for sodium pectinate and $6{\cdot}4 \times 10^4$, $15 \times 10^4$, and $8{\cdot}6 \times 10^4$ respectively for the three samples of sodium carboxymethyl cellulose.
W. J. M.

**Chemistry of the Formation of Organopolysiloxanes.** K. A. Andrianov and N. N. Sokolov. *Doklady Akad. Nauk S.S.S.R.*, **82**, 909–912 (21 Feb. 1952).

The vapours of various organopolysiloxanes $[R_2Si{\cdot}O]_n$ are introduced into the mass spectrograph. The formation under these conditions of the previously unknown monomeric dialkylsilanones $R_2SiO$ is established. The products of the hydrolysis of dimethyldichlorosilane are introduced into the mass spectrograph, and the presence of dimethylsilanone, dimethylsilanediol, and dimethylchlorosilanol is established. It is considered that silicone polymers are formed from the hydrolysis product $R_2Si(OH)_2$ of the dichlorodialkylsilane or dialkoxydialkylsilane used as starting material by two reactions: polycondensation with loss of water, and dehydration to the unstable silanone, which then polymerises. Under conditions of full hydrolysis, the second reaction is the more important. This mechanism accounts for the highly polydisperse character of the polymers obtained.
A. E. S.

PATENTS

**Dispersing and Emulsifying Compositions.** L. A. Gruenwald. *USP* 2,584,123

A mixture of proteinaceous material (65–105 parts by wt.), e.g. partly hydrolysed keratin, an aliphatic or a cyclic nitrogenous compound (100–250), e.g. ethylenediamine, and a drying oil or a fatty acid thereof (0–500) is an excellent dispersing agent for preparing both oil-in-water and water-in-oil emulsions.
C. O. C.

**Homogeneous Liquid Phosphate Detergent.** Stamford Chemical Co. *USP* 2,581,677

A liquid detergent readily soluble in water comprises 5–30% of an alkali-metal phosphate, preferably a poly- or pyro-phosphate, several synthetic organic detergents having synergistic properties, an alkali-metal aryl-sulphonate, and water. When a polyphosphate forms part of the composition, its value as measured by $Ca^{++}$ sequestration does not dissipate on storage, although it is present in aqueous solution.
C. O. C.

**Cleansing Compositions for Mechanical Washing.** General Aniline. *BP* 671,358

A detergent composition comprises 3–30% by wt. of a highly foaming polyglycol ether or thioether of formula $R{\cdot}Z{\cdot}(CH_2{\cdot}CH_2{\cdot}O)_x{\cdot}H$ (R = aliphatic hydrocarbon radical of > 3 C or aryl substituted by such a radical; Z = O or S; $x$ = 6–100) (*BP* 380,431: J.S.C.I., **48**, 332 (1932)), 2–10% of an alkali-metal soap, 3–30% of an alkali-metal pyrophosphate, 1–10% of a corrosion and stain inhibitor (e.g. *NN'*-tetracarboxymethylethylenediamine), and the remainder water. The product combines excellent detergent and ion-sequestering properties, but does not foam sufficiently to impede liquid flow in machines.
J. W. B.

**Surface-active Agents.** Universal Oil Products Co. *BP* 671,353

Benzene or a monoalkylbenzene (Alk of < 5 C) is treated, in presence of a liquid acid alkylation catalyst, e.g. $H_2SO_4$ or HF, with a long-chain mono-olefin of b.p. 160–320° C., consisting of propylene polymers of 12–18 C per mol. The alkylbenzenes formed are sulphonated, and then neutralised to obtain surface-active alkylbenzene-sulphonates.
J. W. B.

**Surface-active Sulphation Products.** N.V. De Bataafsche Petroleum M. S. *BP* 671,833

Sulphation products useful as detergents and wetting agents are prepared by treatment of alkenes of 6–8 C, e.g. 1-hexene, with water gas in an autoclave in presence of a cobalt catalyst followed by catalytic hydrogenation. After distilling off unchanged hydrocarbon and keto-alcohols, a thick oily residue remains, which is sulphated and neutralised to a water-sol. salt.
J. W. B.

**Surface-active Sulphonated Compounds—Detergents and Wetting Agents.** Procter & Gamble Co. *USP* 2,584,701

The sulphonation products of compounds of formula $R{\cdot}CO{\cdot}X^1{\cdot}C_nH_{2n}{\cdot}CO{\cdot}X^2{\cdot}Y$ (R·CO = acyl group of a sat. fatty acid of 8–22 C; $n$ = 1–3; $X^1$ and $X^2$ = O or NZ; Z = H or Alk of < 4 C; Y = alkenyl of 3–4 C) are detergent and wetting agents which are effective in soft, hard, or salt water and in dilute acid or alkali.
C. O. C.

**Stable, Solid, Water-soluble, Surface-active Compositions containing Urea and a Quaternary Ammonium Compound.** Mathieson Chemical Corpn. *USP* 2,584,056

A mixture of (i) not > 80% by wt. of urea, (ii) a water-soluble surface-active compound containing at least one chain of 8–16 C in a quaternary ammonium radical (12–22% on the wt. of urea), and (iii) sodium acetate (4·0–6·5% on the combined wt. of (i) + (ii)) can be fused at superatmospheric pressure and not > 110° C. to a homogeneous melt.

*USP* 2,584,057

A mixture of (i) urea (95% by wt.), (ii) quaternary ammonium compound of the above type (3–45% on the wt. of urea), and (iii) glacial acetic, syrupy phosphoric, or conc. sulphuric acid (2–12% on wt. of (i) + (ii)) fuses at

superatmospheric pressure and 110–150° C. to a homogeneous melt. C. O. C.

**Silylphenoxyalcohols Emulsifiers and Detergents.** Dow Corning Corpn. *USP 2,584,751*

The compounds $n$ or $p$-$Si(CH_2)_xC_6H_4O(CH_2CHR\cdot O)_yH$ ($R$ = H or $CH_3$) are useful as emulsifiers and detergents. C. O. C.

**Quaternary Ammonium Higher Alkarylsulphonates.** Société Anonyme d'Intoxications Chimiques dite: Stancva ou Sadic. *BP 673,842*

Preparation of compounds of formula—

$$[R^1R^2R^3A\cdot SO_3]$$

($R^1$ = Alk of 1–7 C; $R^2$ = Alk of ⩾ 7 C; A = subst. or unsubst. Ar which may contain one benzene ring or several condensed benzene rings; $R^3$ = tertiary aromatic or heterocyclic amine) is described. They are cation active detergents having bactericidal and fungicidal properties. C. O. C.

**Acid and Quaternary Salts of Polyamides Foam-inhibiting Agents.** Dearborn Chemical Co. *USP 2,583,772*

Compounds of formula—

$$R^1CO\cdot NH[A^1\cdot NY]_p A^2\cdot NR^2Z^1[X\cdot Alk]_q$$
$$[A^2\cdot NY]_m[A^3\cdot NR^2Z^2(X\cdot Alk)_q]_n A^3\cdot NH\cdot CO\cdot R^3$$

($R^1$ and $R^3$ = hydrocarbon groups of ⩾ 10 C; $R^2$ = subst. or unsubst. Alk or alkoxy; $A^1$–$A^3$ = alkylene; X = a mineral acid anion; Y = H or acyl; $Z^1$ and $Z^2$ = H or Alk; $m$, $n$, and $p$ = 0, 1, or 2; $q$ = 0 or 1) are dispersible in water and useful as foam inhibiting agents. C. O. C.

**Textile Lubricating and Conditioning Agents.** Celanese Corpn. of America. *BP 672,286*

A good lubricant, which renders fibres, especially acetate rayon, completely antistatic, consists of mineral oil of Saybolt viscosity 45–100 (50–70 parts by wt.), a partial ester of phosphoric acid with a long-chain aliphatic alcohol, e.g. primary n-decyl phosphate (5–15), a condensate formed from a hydroxyalkylamine and a long-chain aliphatic acid with loss of water, e.g. diethanolamino-ethyl ester of coconut oil fatty acids (10–30), a hydroxyalkylamine, e.g. triethanolamine (1–4), and an alkylphenol, e.g. 2,4-di-*tert*.-amylphenol (1–4). C. O. C.

**Antistatic Treatment of Vinyl Resins.** American Cyanamid Co. *USP 2,581,836*

Compounds of formula—

$$NH_2\cdot CO\cdot NH\cdot C(NH_2)\cdot NH_2SO_3Alk$$

particularly those in which Alk has 12–18 C, are excellent antistatic agents for vinyl resin filaments, films, etc. C. O. C.

**Divinyl Sulphones as Tanning Agents and for Rendering Wool Alkali-resistant.** United States Rubber Co. *USP 2,579,871*

Animal and vegetable proteins treated with vinyl sulphone have good stability to heat, water, solvents, and alkali. Thus wool treated with vinyl sulphone can be dyed in alkaline vats. Leather tanned with vinyl sulphone has improved stability. The action of vinyl sulphone takes place readily at room temperature. C. O. C.

**Polyalkylenepolyaminoalkylcarboxylic Acids for Preventing Precipitates in Azoic Padding Liquors.** J. M. Danner and W. Zerweck. *BP 671,979*

Compounds of formula—

$$R_2N[Alkylene\cdot NR]_xAlkylene\cdot NR_2$$

(at least one R = carboxyalkyl, the other R = H or two of them together = alkylene; $x$ = 1–7) added to azoic padding liquors stabilise them so that there is no precipitate even on standing for several days. C. O. C.

**Resin Finishing Liquors.** Monsanto. *BP 672,130*

Use of a hydroxyalkylamine salt of an inorganic acid as the catalyst for halogenated amino aldehyde condensates greatly improves the stability of their solutions or dispersions and enables 25–30% dispersions to be made which can be diluted to 5–15% strength after standing for 24 hr. C. O. C.

**Dispersions of Polymeric Tetrafluoroethylene.** DuP. *BP 673,443*

Aqueous colloidal dispersions of polymeric tetrafluoroethylene are obtained by polymerising the monomer in aqueous solution in presence of a water-soluble polymerisation catalyst and 0·1–12·0% on the wt. of the water of a sat. hydrocarbon of ⩾ 12 C which is liquid under the polymerisation conditions. Presence of these hydrocarbons enables great increase in the concentration of colloidal polytetrafluoroethylene in the dispersion before coagulation starts. These dispersions may be used for rendering textiles water-repellent, casting into films, etc. C. O. C.

**Organosilicon Water-repellent Agents.** Dow Corning. *BP 671,773*

Compounds of formula $[SiR_2SiR_2CH_2]_n$ (R = Alk or Ar; $n$ = 1) are useful water-repellent agents. C. O. C.

**Polydimethylsiloxanediols Waterproofing Agents.** Dow Corning. *BP 671,579*

Polydimethylsiloxanediols of formula—

$$HO[Si(CH_3)_2O]_nH$$

($n$ = 5–61) are useful waterproofing agents. C. O. C.

**Organosilicon Copolymers Water-repellent Agents.** Dow Corning. *BP 671,140*

Siloxane copolymers containing Si atoms bonded to O of siloxane linkages and also Si atoms having all their bonds satisfied by C are useful water-repellent agents. They contain 1·98–2·1 organic radicals per Si attached to O, 50% of the organic radicals being $CH_3$. W. G. C.

**Organosilicon Compounds Water-repellent and Foam-preventing Agents.** Dow Corning. *BP 672,824-5*

Compounds of formula $R\cdot SiY_2\cdot CH_2\cdot SiY_2\cdot R$ (R = Alk or monocyclic Ar; Y = alkoxy or Hal) are useful as water-repellent agents for textiles. Upon hydrolysis and condensation they yield foam-preventing agents. C. O. C.

**Organosilicon Copolymers Foam-preventing Agents.** Dow Corning. *BP 671,722*

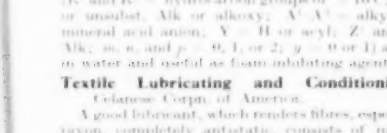
Organosiloxane copolymers, in which the Si atoms are linked in pairs by O atoms and by $CH_2$ radicals so that they contain structures of the type $-Si\cdot CH_2\cdot Si-$ but none of the type $-Si\cdot CH_2\cdot Si\cdot CH_2\cdot Si-$ and in which all other valencies of the Si atoms are satisfied by $CH_3$ radicals, are useful foam-preventing agents. C. O. C.

**Hydro-polyalkoxysilyl Addition Products of Rubber.** Dow Corning. *BP 671,747*

A mixture of a polyolefinic rubber hydrocarbon and a compound of formula $R_mSiHCl_{3-m}$ (R = methyl or phenyl; $m$ = 0 or 1) is kept at 15–400° C. under pressure until the mass becomes liquid, after which it is treated with an alkoxysilane or an alcohol. The products are useful as waterproofing agents, varnishes, and film-forming materials. They may be applied in solution and hydrolysed in contact with cellulosic materials. C. O. C.

**Insect Repellents.** U.S. Secretary of the Army. *USP 2,581,840-1*

Ethyl 6-ethyl 4-keto-2-methyl-2-*cyclo*hexene-1-carboxylate (I) and 4-hydroxy*cyclo*hexyl propionate—



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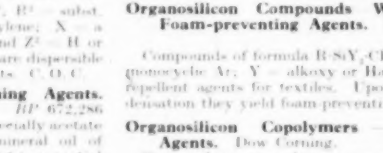
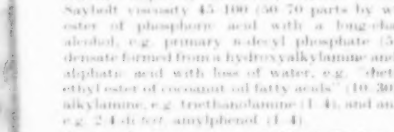


(II)

are highly effective insect repellents; fabrics impregnated with them are repellent to *Aedes aegypti* for at least 10 days. C. O. C.

**Pest-combating Agents.** Gy. *BP 672,971*

Compounds of formula—



($R^2$ and $R^3$ = H or $CH_3$; $R^3$ and $R^4$ = sat. or unsat. Alk of 1–5 C) are very efficient pest-combating agents. Thus textiles impregnated with a 20% soln. of 5:5-dimethyldihydroresorcinol diethylcarbamate in isopropyl alcohol are given long-lasting repellency to insects. C. O. C.

**Cellulose Sulphamylethyl Ether.** Hercules Powder Co. *USP* 2,580,351

Sulphamylethyl celluloses, obtained by treating cellulose with a vinylsulphonamide in presence of alkali, are soluble in aqueous alkalis and do not form insoluble salts in hard water. They have suspending, thickening, stabilising, and film-forming properties, making them useful as detergents, thickening agents for printing pastes, etc. C. O. C.

**Sulphoethyl Ethers of Polysaccharides.** Hercules Powder Co. *USP* 2,580,352

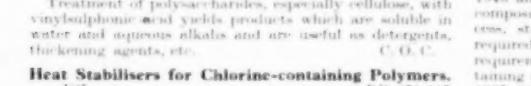
Treatment of polysaccharides, especially cellulose, with vinylsulphonic acid yields products which are soluble in water and aqueous alkalis and are useful as detergents, thickening agents, etc. C. O. C.

**Heat Stabilisers for Chlorine-containing Polymers.** ICI. *BP* 671,647

Semicarbazide and its condensation products are good heat stabilisers for chlorine-containing polymers. C. O. C.

**Blue-fluorescent Dyes—Optical Bleaching Agents.** DuP. *USP* 2,581,057

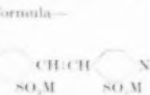
Compounds of formula—



(M = H or other suitable cation, e.g. Na or pyridinium) have pronounced bluish fluorescence under ultraviolet radiation and are substantive to cellulose. C. O. C.

**Ultraviolet-absorbing Compounds.** General Aniline. *BP* 671,857

Compounds of formula—



(one R = H, the other R = $SO_3M$; M = alkali metal, alkaline earth metal, or salt-forming radical) absorb ultraviolet radiation of 200–400 mμ. They can be used for coating or impregnating materials which fade or deteriorate when exposed to sunlight. C. O. C.

I.G. Farbenindustrie A.-G., Hoechst a. M.—Reports and Instructions on Preparation of Dyes, Intermediates, and Auxiliary and Finishing Agents (IV this page).

Methin Dyes and Optical Bleaching Agents containing Coumarin Nuclei (IV p. 321).

Modified Urea–Formaldehyde Resin for Paper Sizing (XI p. 330).

## IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

**Colour and Molecular Structure. I—Correction of Herzfeld's Theory of the Effect of Substitution on Absorption Position.** H. Baba and S. Nagakura. *J. Chem. Soc. Japan, Pure Chem. Sects.*, **72**, 72–74 (1951); **II—Several Types of Relation between Substitution and Wavelength Shift.** H. Baba. *Ibid.*, 74–77; *Chem. Abs.*, **46**, 3857 (10 May 1952).

**I**—Criticism of Herzfeld's theory on the wavelength shift of a conjugated double-bond system by substitution. The number of electrons migrating from a substituent to a conjugated system is two, and, as each molecular orbital can take two electrons of opposite spin, even if an electron migrates from an orbital *n* to *m*, the orbital *m* is only half filled, and hence cannot be excluded from the electron-migration effect entirely, while the orbital *m* [*sic*], which still remains half filled, must be different from a completely empty orbital. Herzfeld's theory is amended to meet these facts.

**II**—Electronic transitions in conjugated double-bond systems are of two types: π–π and l–π, in which an electron (other than a π-electron) belonging to a non-bonded electron pair at an atom in the conjugated system jumps into an empty π-electron level. C. O. C.

**I.G. Farbenindustrie A.-G., Hoechst a. M.—Reports and Instructions on Preparation of Dyes, Intermediates, and Auxiliary and Finishing Agents.** FD 545/51* (PB 73,484; Reel A 36).

A microfilm of 148 reports and instructions, in German, dated 1934–1946, dealing with the manufacture of dyes, intermediates, and auxiliary and finishing agents including developments in the plant used.

FD 500/51* (PB 74,067; Reel CC 122).

Replies, in English, to a questionnaire completed in 1946 and giving, for 364 individual items, the chemical composition, principal use, plant required, working process, standardisation, raw materials and intermediates required, by-products produced, and heat and power requirements. In addition there are several tables containing information on various chemicals produced during 1937–44. C. O. C.

*Photocopies available from T.I.D.C., D.S.I.R., Canard Building, 15 Regent Street, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.—see *J.S.D.I.*, **66**, 33 (Jan. 1950).

**Alleged Beckmann Rearrangement of Quinone Monoxime.** R. A. Raphael and E. Vogel. *J.C.S.*, 1958–1959 (May 1952).

Instead of the alleged rearrangement of quinone monoxime by benzenesulphonyl chloride in pyridine to an aza-γ-tropolone, it is found that the reaction product is *pp'*-didihydroxyazoxybenzene. H. H. H.

**Nitration of Esters of 4-Hydroxydiphenyl. Preparation of 4-Hydroxy-4- and -2-nitrodiphenyls.** B. Jones and F. Chapman. *J.C.S.*, 1829–1832 (May 1952).

The nitration in acetic acid is described of the benzoate, benzenesulphonate, toluene-*p*-sulphonate, and acetate of 4-hydroxydiphenyl, and it is established that substantial amounts of the 2-nitro esters are formed mixed with the 4-nitro isomerides. An improved method for the preparation of 4-hydroxy-4-nitrodiphenyl is included. H. H. H.

**Improved Synthesis of 4-Bromo-4-hydroxydiphenyl.** G. W. Gray, J. B. Hartley, and B. Jones. *J.C.S.*, 1959–1960 (May 1952).

Bromination of the esters of 4-hydroxydiphenyl gives only poor yields of 4'-bromo derivatives, but the less direct method, based on the bromination of 4-nitrodiphenyl and its subsequent reduction and diazotisation, has been improved in its later stages to give good yields of pure products on a large scale. H. H. H.

**Chemistry of 4-Nitro-4-aminodiphenyl Sulphone. I—Products of Coupling the Diazotised Sulphone with Phenols and Naphthols.** M. S. Zhudek. *J. Appl. Chem. U.S.S.R.*, **25**, 109–113 (Jan. 1952). **II—Products of Coupling the Diazotised Sulphone with Aromatic Hydroxy Acids.** M. S. Zhudek and S. S. Shtal. *Ibid.*, **25**, 114–116 (Jan. 1952).

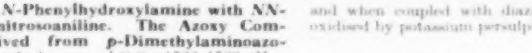
4-Nitro-4'-aminodiphenyl sulphone is prepared, diazotised, and coupled with 33 phenols, naphthols, etc., and 20 aromatic hydroxy acids. The properties, e.g. m.p., colour in acid and alkaline soln., appearance of dyeings on wool and silk, antituberculer activity, of the resulting dyes are tabulated. A number of the dyes are good acid–base indicators. A. E. S.

**Kinetics of the Coupling Reaction—Discussion and Applications of the Kinetic Reaction Equation.** H. Zollinger and C. Wittwer. *Helv. Chim. Acta*, **35**, 1209–1223 (June 1952).

A kinetic equation for the azo coupling reaction is discussed. It contains the concentration of that form of the coupling component which enters the rate-determining step of the reaction, and the reaction rate constant obtained in this way is independent of the acidity of the medium. The results of kinetic measurements with resorcinol and their difference from those with simple phenols are explained by means of this equation. The technically important dependence of the coupling position in aminonaphtholsulphonic acids on the acidity of the medium is interpreted kinetically by the influence of $[H^+]$ on the concn. of the different forms of the aminonaphthol. H. H. H.

**Condensation of *N*-Phenylhydroxylamine with *NN*-Dimethyl-*p*-nitrosoaniline. The Azoxy Compounds derived from *p*-Dimethylaminoazobenzene.** W. Anderson. *J.C.S.*, 1722–1726 (May 1952).

α- and β-*p*-Dimethylaminoazoxybenzene are both obtained on condensation of *N*-phenylhydroxylamine with *NN*-dimethyl-*p*-nitrosoaniline. The course of the reaction is contrary to that generally found for reactions between *N*-arylhydroxylamines and arylnitroso compounds possessing different aryl residues.



α-Isomer β-Isomer

H. H. H.

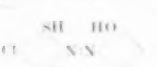
**2-Alkylthioanilines, Alkylthionaphthalenes, and Derived Monoazo Dyes.** R. Specklin and J. Meybeck. *Bull. Soc. chim. France*, 621–626 (1951); *Chem. Abs.*, **46**, 3281 (10 April 1952).

Alkylation of thiophenols, or reaction of a thiol with an *o*-halogenonitrobenzene or an *o*-halogenoiminitrobenzene, followed by Bechamp reduction, gave 2-alkylthioanilines, which can be diazotised and coupled with *ortho*-coupling phenols and naphthols. The azo compounds so produced, e.g. 5-bromo-2-ethylthioaniline→β-naphthol, give copper complexes which dye wool.

Alkylthionaphthalenes, unlike alkylthiobenzenes, couple readily with diazo compounds in glacial acetic acid without cession of the sulphide link. 2:4-Dinitroaniline→2-hydroxyethylthionaphthalene dyes acetate rayon orange, but very slowly. E. S.

**o-Mercapto-o'-hydroxyazo Dyes.** R. Specklin and J. Meybeck. *Bull. Soc. chim. France*, 627–628 (1951); *Chem. Abs.*, **46**, 3282 (10 April 1952).

Freshly prepared *p*-amino-*m*-thiocyanatophenol (Fichter and Beck, *Chem. Abs.*, **6**, 757) can be diazotised and coupled, but after standing for 24 hr. it will not react with $HNO_2$. 4-Chloro-2-methyl-6-thiocyanatoaniline (*Chem. Abs.*, **24**, 2138), prepared at a low temperature to minimise isomerisation, was diazotised with HCl and $NaNO_2$ (the diazotisation is slow), and coupled with alkaline β-naphthol soln. in presence of alcohol. Reduction of the azo dye with NaSH in alcohol gave the disulphide corresponding to the *o*-mercaptoazo dye—



E. S.

**Polyhydroxyethylanilines and Derived Disperse Dyes.** V. Arnould and H. Wahl. *Bull. Soc. chim. France*, 491–493 (1951); *Chem. Abs.*, **46**, 3281 (10 April 1952).

*N*-Ethyl-*N*-(hydroxyethoxyethyl)aniline and *N*-ethyl-*N*-(hydroxyethoxyethoxyethyl)aniline were obtained by passing 1 mol. of ethylene oxide into *N*-ethyl-*N*-hydroxyethylaniline in presence of KOH or pyridine. Trityl and various acyl derivatives of these amines and of *NN*-bis-hydroxyethylaniline are described, and the preparation and properties of disperse dyes made by coupling suitable diazo compounds with the amines are discussed. E. S.

**Researches on Monolayers. II. Effect of Acid and Alkali upon Monolayers of Aromatic Azo Compounds containing Long Alkyl Chains.** C. H. Giles and E. L. Neustadter. *J.C.S.*, 1864–1869 (May 1952).

The apparent molecular areas and compressibilities of aromatic hydroxyazo compounds containing long alkyl chains have been measured in monolayers on dilute acid and alkali. Whereas the *p*-hydroxy compounds appear to exist almost completely in the azo form, the *ortho* compounds contain much of the hydrazone form. Evidence for the presence of the azo form in the latter series is equivocal, except possibly in the case of the *oo'*-dihydroxyazo compounds. H. H. H.

**Some Reactions of Indan-4-ol.** W. Baker, J. F. W. McOmie, and T. L. V. Ulbricht. *J.C.S.*, 1825–1829 (May 1952).

Indan-4-ol (I) reacts in positions 5 and 7 when nitrated and when coupled with diazotised *p*-nitroaniline; it is oxidised by potassium persulphate to indane-4:7-diol (II).



(I) (II)

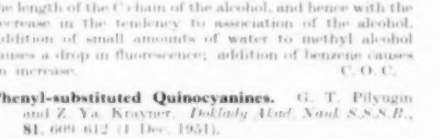
H. H. H.

**Solvatochromy.** E. Suhrmann and H. H. Perkampus. *Naturwissenschaften*, **38**, 382 (1951); *Chem. Abs.*, **46**, 3855 (10 May 1952).

Pigments of the type of 1:2:4-trimethyl-3-hydroxyphenazine change colour depending on the solvent. They are dark red in acetic acid, red in alcohols, yellow in benzene, and light yellow in ethyl acetate. This is due to the intensity of the absorption band at 19,000 cm.$^{-1}$; its extinction coefficient increases twentyfold from ethyl acetate to acetic acid. Hydrogen bond formation between solvent and oxygen in the pigment causes this, as is indicated by the fluorescence of the pigment. In acetic acid fluorescence is negligible, but in alcohols it increases with the length of the C chain of the alcohol, and hence with the decrease in the tendency to association of the alcohol. Addition of small amounts of water to methyl alcohol causes a drop in fluorescence; addition of benzene causes an increase. C. O. C.

**Phenyl-substituted Quinocyanines.** G. T. Pilyugin and Z. Ya. Kraytner. *Doklady Akad. Nauk. S.S.S.R.*, **81**, 609–612 (1 Dec. 1951).

A general method is evolved for the preparation of *N*-aryl quaternary salts of quinaldine and its derivatives. It consists in the treatment of the hydrochloride of diphenylamine or one of its derivatives with paraldehyde, and it is applied to the synthesis of some of the previously unknown phenylquinocyanines, viz.



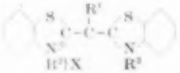
The absorption max. of each unsymmetrical dye is compared with the mean of the values for the two corresponding symmetrical dyes, and the *N*-phenyl compounds are compared with the corresponding *N*-ethyl compounds. The unsymmetrical dyes show a hypsochromic shift from the calc. absorption max.; it is particularly high for the styryl dye (66 mμ.). Replacement of *N*-ethyl by *N*-phenyl leads to a bathochromic shift (6·5–19 mμ.). A. E. S.

**Derivatives of Dibenzothiazolylmethane.** A. I. Kiprianov, L. P. Yakovleva, and Yu. S. Rozum. *J. Gen. Chem. U.S.S.R.*, **22**, 302–309 (Feb. 1952).

Dibenzothiazolylmethane and derivatives in which one H of the methane residue is replaced by alkyl or aryl are shown to be tautomeric in soln.—

(I) (II)

Five new compounds are prepared ($R^1 = CH_3$, $C_2H_5$, $nC_3H_7$, $CH(CH_3)_2$, $C_6H_5$), and their tautomerism is studied by comparing the absorption spectra of their alcoholic solutions in the ultraviolet region with the spectra of a cpd. with the bond system I (replace H by $R^1 = CH_3$) and a cpd. with the bond system II ($R^1 = H$; replace H by $CH_3$). The derived thiacyanines—



$R^2X$ $R^2$

are examined, and it is shown that in a series of dyes in which either R¹ or R² is H, the other being alkyl, the absorption max. and extinction coeff. do not vary appreciably, but if both R¹ and R² are alkyl groups, the max. is found at a longer wavelength with a much lower extinction coeff. It is concluded that in these molecules steric hindrance leads to a disturbance of the coplanarity of the thiazole rings. A. E. S.

**Cyanine Dyes. V—Thiacyanine Dyes containing Thiourea Groupings.** N. F. Turitsyna and I. I. Levkoev. *J. Gen. Chem. U.S.S.R.*, **22**, 309–321 (Feb. 1952).

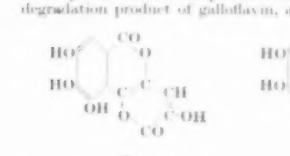
In an attempt to combine the general chemical sensitising effect on the photographic emulsion of thiourea and its derivatives with the photosensitising effect of the cyanine dyes, 24 new thiacyanines containing thiourea side-chains (·NH·CS·NH·Alk and ·NH·C(S·Alk):N·Alk) are prepared. However, the dyes do not show chemical sensitising properties. A. E. S.

**Sulphonation of Quinones.** A. P. Terentyev and A. N. Grinev. *Doklady Akad. Nauk S.S.S.R.*, **81**, 617–619 (1 Dec. 1951).

Direct sulphonation of benzoquinone, naphthaquinones, and their derivatives has not yet been achieved. The action on benzoquinone of sulphur trioxide in the form of its double cpd. with pyridine or dioxan is examined. Treatment with the dioxan cpd. at room temp. for 2–3 days leads to the formation of the hitherto unknown 1:2:4-trihydroxybenzene-3-sulphonic acid. Tolnquinone reacts in analogous fashion. 1:4-Naphthaquinone yields a disulphonated trihydroxynaphthalene having one sulpho group in each nucleus. A. E. S.

**Galloflavin I.** R. D. Haworth and J. M. McLachlan. *J.C.S.*, 1583–1589 (May 1952).

The preparation of galloflavin by aeration of alkaline solutions of gallic acid has been improved, the earlier degradative work of Herzig *et al.* has been largely confirmed and extended, and new formulæ (I and II) are proposed for gallofiavin and *iso*gallofiavin respectively. Two syntheses of 3-acetyl-4:5:6-trimethoxyphthalide, a degradation product of gallofiavin, are described.



(I) (II)

H. H. H.

**Polarographic Investigation of the Redox Behaviour of Certain Hydroxy and Sulphonic Acid Derivatives of Anthraquinone.** R. Gill and H. I. Stonehill. *J.C.S.*, 1845–1857 (May 1952).

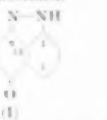
The redox potential $E$ and semiquinone formation constant $K$ are determined polarographically at 25° C. for aqueous solutions of the 1- and 2-sulphonic acids and the 1- and 2-hydroxy and 1:2-, 1:4-, 1:8-, and 2:6-dihydroxy derivatives of anthraquinone over the pH range 7–13 at constant ionic strength. The reversibility of the polarographic oxidation–reduction is demonstrated, except for the 2-hydroxy and 2:6-dihydroxy compounds, which tautomerise in the reduced state (see following abstract). Semiquinone formation is favoured by increased ionisation at high pH, while not completely absent at the lowest pH used. The influence of the substituent groups on $E$ and $K$ for the fully ionised compounds is explained in terms of inductive, resonance, and *ortho* effects. Addition of ethanol renders $E$ more negative, increases $K$, and decreases diffusion current constant, while increase of ionic strength at constant pH in aqueous solutions renders $E$ more negative and decreases $K$. There is no evidence for association or polymerisation. H. H. H.

**Polarographic Investigation of the Tautomerism of 2-Hydroxy- and 2:6-Dihydroxy-anthraquinol.** R. Gill and H. I. Stonehill. *J.C.S.*, 1857–1863 (May 1952).

Over a certain pH range for each, 2-hydroxy- and 2:6-dihydroxy-anthraquinol give polarographic oxidation waves which decrease in height with time, owing to reversible tautomerisation to the corresponding oxanthrols. It is deduced that the particular state of ionisation of the quinol responsible for the tautomerisation is that in which only one of the three hydroxy groups is ionised. In 1:2-dihydroxyanthraquinol the 1-hydroxy group prevents tautomerisation by causing hydrogen bonding in the quinol and steric hindrance in the oxanthrol. H. H. H.

**1:9-Pyrazoloanthrone. I—Replacement of Halogens in Derivatives of 1:9-Pyrazoloanthrone.** W. Bradley and K. W. Geddes. *J.C.S.*, 1630–1635 (May 1952).

The 2- and 3-bromo and 4-, 5-, and 8-chloro derivatives of 1:9-pyrazoloanthrone (I) are prepared, and their behaviour towards aniline, piperidine, and sodium methoxide is described. The relation between orientation and ease of replacement of a substituent is similar to that in the *meso*benzanthrone series. The two *N*-methyl derivatives of I are also described.



(I) H. H. H.

**1:9-Pyrazoloanthrone. II—Nuclear Substitution by Bases and Self-condensation in 1:9-Pyrazoloanthrone and its *N*-Methyl Derivatives.** W. Bradley and K. W. Geddes. *J.C.S.*, 1636–1643 (May 1952).

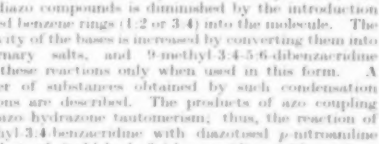
1:9-Pyrazoloanthrone and its *N*-methyl derivatives readily undergo nuclear substitution by reactive anions, e.g. that of sodium anilide, the substituting anion entering the indazole nucleus and replacing the hydrogen in *para*-position to the CO group. 1'-Methylpyrazolo[3':4':5':1:13:9]anthrone is more easily substituted than the isomeric 1'-methylpyrazolo[5':4':3':1:13:9]anthrone, a difference attributed to bond-fixation, which results in a higher degree of unsaturation in the first isomer. These compounds also undergo self-condensation in the presence of bases, and are hydrolysed by fused alkalis. H. H. H.

**Condensation Reactions of 9-Methylbenzacridines. I—Reactions of 9-Methyl-3:4-benzacridine.** A. E. Porai-Koshits and G. S. Ter-Sarkisyan. *Izvestiya Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 600–609 (Sept.–Oct. 1951); **II—Reactions of 9-Methyl-1:2-benzacridine and of 9-Methyl-3:4-5:6-dibenzacridine.** Idem. *Ibid.*, 771–776 (Nov.–Dec. 1951).

Contrary to expectations, the readiness with which the methyl of 9-methylacridine undergoes condensation with aromatic aldehydes, with *p*-nitrosodimethylaniline, and with diazo compounds is diminished by the introduction of fused benzene rings (1:2 or 3:4) into the molecule. The reactivity of the bases is increased by converting them into quaternary salts, and 9-methyl-3:4-5:6-dibenzacridine gives these reactions only when used in this form. A number of substances obtained by such condensation reactions are described. The products of azo coupling show azo–hydrazone tautomerism; thus, the reaction of 9-methyl-3:4-benzacridine with diazotised *p*-nitroaniline and that of 9-aldehydo-3:4-benzacridine with *p*-nitrophenylhydrazine yield identical products—a red substance. A. E. S.

**Polynuclear Heterocyclic Systems. V—5:8-Diazapentaphene.** G. M. Badger and R. Pettit. *J.C.S.*, 1874–1877 (May 1952).

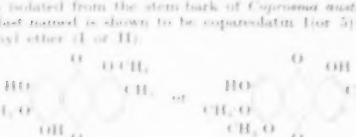
Cyclisation of *p*-phenylenedianthranilic acid gives the angular quinacridone (I), which is oxidised by nitric acid in acetic acid to 5:8-diazapentaphene (II). Oxidation of II with selenium dioxide gives 2:3-6:7-dibenzo-1:8-diazafluorenone.



(I) (II) H. H. H.

**Chemistry of the *Coprosma* Genus. VI—Minor Anthraquinone Colouring Matters from *Coprosma australis*** L. H. Briggs, G. A. Nicholls, and R. M. L. Paterson. *J.C.S.*, 1718–1722 (May 1952).

Three further compounds—soranjidiol, rubiadin, and a new dihydroxymethoxymethylanthraquinone—have been isolated from the stem bark of *Coprosma australis*; the last named is shown to be coparvadatin [1or 5]-6-dimethyl ether (I or II):



(I) (II)

H. H. H.

**Effect of the Medium on the Photochemical Reduction by Organic Acids of Chlorophyll, Riboflavine, and other Colouring Matters.** A. A. Krasnovsky and V. A. Gavrilova. *Doklady Akad. Nauk S.S.S.R.*, **81**, 1105–1108 (21 Dec. 1951).

To a soln. of a colouring matter (chlorophyll, riboflavine, β-carotene, magnesium phthalocyanine, phenol indophenol, Safranine T, or Neutral Red) in pyridine, dioxan, ethanol, or water a reducing agent (ascorbic, pyruvic, citric, malic, or succinic acid) is added, and the system evacuated. On irradiation, photochemical reduction occurs in many cases. It is found that the course of the reaction and the position of any photochemical equilibrium that is established depend greatly on the nature of the medium, as well as on the nature of the reacting substances. A. E. S.

**Changes in the Fluorescence Spectra of Magnesium Phthalocyanine and of Chlorophyll due to Dark Reactions.** V. F. Gachkovsky. *Doklady Akad. Nauk S.S.S.R.*, **82**, 739–742 (11 Feb. 1952).

When magnesium phthalocyanine is adsorbed from its soln. in ethanol, ether, acetone, or pyridine on to MgO, the fluorescence spectrum of the immediate product varies with the solvent used, but after a time the original spectrum disappears and is replaced in each case by one with a max. at 684 mμ. Under vacuum conditions, if the oxygen complex is formed and the vapour of one of the above solvents is then admitted, the original fluorescence spectrum is immediately replaced in each case by one with a max. at 666 mμ; but if the solvent complex is formed and oxygen then admitted, the spectrum characteristic of the solvent persists. When water vapour is admitted to the oxygen complex, the 666 mμ. band is formed immediately, but it slowly gives way to the 684 mμ. band. It is suggested that the oxygen complex is very reactive and is able to remove H from many substances, forming a complex with an OOH radical. When formed on an anhydrous substrate, this has a fluorescence max. at 666 mμ., but in presence of water the MgO substrate becomes hydrated, leading to a shift in the max. to 684 mμ. Precisely similar phenomena are observed for chlorophyll. A. E. S.

**Photoelectrochemical Effect of Phthalocyanines, Chlorophyll, and Phæophytin.** V. B. Evstigneev and A. N. Terenin. *Doklady Akad. Nauk S.S.S.R.*, **81**, 223–226 (11 Nov. 1951).

It is considered that the measurement of the photoelectrochemical effect of pigments—the changes due to exposure to light in the potential of an inert electrode covered with a layer of the pigment and immersed in a soln. containing electrolyte and other substances—will provide a powerful method for the investigation of the photochemical behaviour of pigments with oxidation-reduction properties. The experimental procedure is described, and the behaviour of phthalocyanine, chlorophyll, and phæophytin is discussed and illustrated graphically. A. E. S.

**Absorption Spectra of Chlorophyll in Solutions at Low Temperatures. Equilibrium between Isomers.** S. Freed and K. M. Sancier. *Science*, **114**, 275–276 (1951); *Chem. Abs.*, **46**, 3855 (10 May 1952).

The absorption spectra of chlorophylls a, b, and b′ in a 20 : 40 : 40 by vol. mixture of dipropyl ether, propane, and propene at 75–230 k. and in 20 : 80 dipropyl ether–hexane at 230–300 k. indicate that there are at least two components in chlorophyll b. The differences in the spectra of the chlorophylls in different solvents may be largely due to change in the relative concentrations of isomers present in equilibrium. C. O. C.

**Ultraviolet Spectrum of Naringin by Use of the Beckmann Model DU Spectrophotometer.** C. D. Douglass, T. B. Gage, and S. H. Wender. *Proc. Oklahoma Acad. Sci.*, **29**, 67–70 (1948); *Chem. Abs.*, **46**, 3856 (10 May 1952).

The ultraviolet absorption spectrum of purified naringin shows maxima at 285 and 330 mμ. C. O. C.

**Solubilisation of Flavonoids. I—Solubilisation of Rutin and Quercetin.** M. Shimizu, M. Kiriyawa, and H. Ogawa. *J. Pharm. Soc. Japan*, **71**, 875–879 (1951); **II—Partial Methylation of Rutin and Quercetin with Diazomethane.** M. Shimizu and G. Ohta. *Ibid.*, 879–882; **III—Solubilisation Mechanism.** M. Shimizu. *Ibid.*, 882–885; **IV—Extraction of Rutin from *Flos sophoræ japonicæ*.** M. Shimizu and G. Ohta. *Ibid.*, 885–888; *Chem. Abs.*, **46**, 4004 (10 May 1952).

**I**—Rutin is soluble to the extent of 198.5 mg. in 10 ml. in aq. soln. containing 0·028 g. NaOH + 0·704 g. $H_3BO_3$ in 100 ml.

**II**—Results of methylation indicate that rutin and quercetin form bonds at two places with $NaH_2BO_3$.

**III**—Results of methylation and the solubility of rutin in aq. NaOH–$H_3BO_3$ indicate formation of two kinds of $H_3BO_3$ complex salts, existing as soluble salts in equilibrium, by bonding of $H_3BO_3$ with the phenolic 3-OH and 5-OH groups and with the 5-OH and the CO of the pyrone ring. This applies also to quercetin. Lake formation of flavonols with heavy-metal oxides is due to formation of an insoluble complex salt. C. O. C.

**Flavone Pigments.** R. Paris. *Produits pharm.*, **6**, 543–549, 606–613 (1951); *Chem. Abs.*, **46**, 4004 (10 May 1952).

A review of the occurrence, extraction, physical and chemical properties, and analysis of the flavones. 111 references. C. O. C.

**Syntheses in the Carotenoid Series. XXI—Condensation of Carotenoid Ketones and Aldehydes with Diacetylene: Another Synthesis of β-Carotene.** H. H. Inhoffen, F. Bohlmann, H. J. Aldag, S. Bork, and G. Leubner. *Annalen*, **573**, 1–16 (1951); *Chem. Abs.*, **46**, 3985 (10 May 1952).

PATENTS

**Mono- and Poly-amides of Alkylenecimines and Acetoacetic Acid.** General Aniline. *BP* 671,917

A wide variety of polymers may be obtained by acylating a polymeric alkyleneimine with diketen or by treating a monomeric alkyleneimine with diketen and allowing the product to polymerise. The products, particularly those which are soluble, are capable, as a result of their containing an activated methylene group, of azo and azomethin formation and so are of use in colour photography. C. O. C.

**Azo-substituted Colour Formers.** General Aniline. *USP* 2,584,349

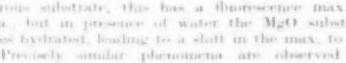
Compounds of formula Ar-N:N-R (R = an organic substituent containing a colour-forming group, e.g. active methylene or hydroxydivinyl, directly attached to the azo group) react in colour-forming development with the oxidation product of the developer to form dyes, the azo group being displaced by the arylamino group. C. O. C.

**Acetals of Polyvinyl Alcohol Colour Formers.** DuP. *BP* 671,713

See also *USP* 2,562,528 (*J.S.D.C.*, **68**, 192 (May 1952)).

**Therapeutic Dye.** Maltine Co. *USP* 2,580,251

The scarlet dye, 1-*p*-carbethoxyphenylazo-2:4-phenylenediamine—



is a highly effective urogenital analgesic. C. O. C.

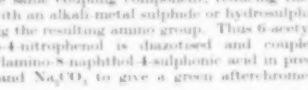
**Metallisable Monoazo Wool Dyes.** Ciba. *BP* 672,734

m-Dihydroxyazo dyes 6-acylamino-2-amino-4-nitrophenol → 1-phenylamino-8-naphthol-4-sulphonic acid may

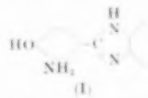
be metallised (especially with chromium compounds) in substance or preferably on the fibre. The same dyes may be made by coupling diazotised 2-amino-4:6-dinitrophenol with the same coupling component, reducing the 6-nitro group with an alkali-metal sulphide or hydrosulphide, and acylating the resulting amino group. Thus 6-acetylamino-2-amino-4-nitrophenol is diazotised and coupled with 1-phenylamino-8-naphthol-4-sulphonic acid in presence of NaOH and $Na_2CO_3$ to give a green afterchrome dye. E. S.

**Copper-complex Direct Cotton Stilbene Azo Dyes.** Ciba. *BP* 671,762

Mainly brown direct cotton dyes are made by coppering in substance stilbene azo compounds—



(X = H or O·CH$_3$; Y = NO$_2$ or the residue of a suitable *p*-aminomonoazo compound; Z = an azo or azoxy group). Thus, all parts being by weight, *o*-phenylenediamine (54) is condensed with *p*-hydroxy-*m*-nitrobenzoyl chloride (101) in chlorobenzene (500) and pyridine (118) to yield 2-*p*-hydroxy-*m*-nitrophenylbenzimidazole, from which the amino compound—



(I)

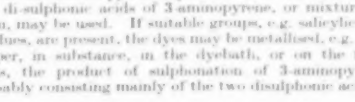
is produced by reduction in presence of an Ni catalyst. I (24·1) is diazotised, and coupled with *m*-anisidine (12·3) in presence of acetic acid, and the resulting aminomonoazo compound is boiled with disodium 4:4′-dinitrostilbene-2:2′-disulphonate (24) and water (1000), to which has been added 30% aq. NaOH (100), for 24 hr. Coppering is carried out in presence of ammonia and ethanolamine at 90–95° C., with elimination of CH$_3$ from the O·CH$_3$ group, to give a violet-brown direct cotton dye. E. S.

**Imbibition Printing using Yellow Disazo Dyes.** Technicolor Motion Picture Corpn. *USP* 2,583,076

The disazo dyes formed by coupling a tetrazotised 4:4′-diaminostilbene with 2 mol. of an acetoacetanilide when used in imbibition printing yield highly transparent yellow images with spectral absorption characteristics particularly suited to the requirements of three-colour work. C. O. C.

**Direct Cotton Disazo Dyes from 3-Aminopyrene-sulphonic Acids.** Ciba. *BP* 672,454

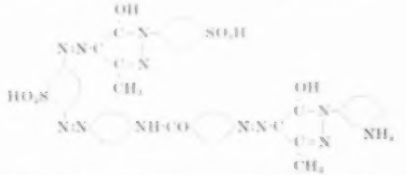
Direct cotton dyes are made when an aminoazo compound 3-aminopyrenesulphonic acid → *p*-coupling primary benzenoid amine is linked by means of phosgene, cyanuric chloride, or 2:4-dichloroquinazoline with a suitable aminomonoazo compound, preferably also derived from a diazotised 3-aminopyrenesulphonic acid. Various mono- and di-sulphonic acids of 3-aminopyrene, or mixtures of them, may be used. If suitable groups, e.g. salicylic acid residues, are present, the dyes may be metallised, e.g. with copper, in substance, in the dyebath, or on the fibre. Thus, the product of sulphonation of 3-aminopyrene, probably consisting mainly of the two disulphone acids—



is diazotised and coupled with *p*-cresidine under weakly acid conditions. Two mol. of the aminomonoazo dye so formed are linked together by treatment of an aqueous, alkaline suspension with phosgene, to form the symmetrical urea. It dyes cellulose fibres bright red. E. S.

**Direct Cotton Trisazo Dyes.** Ciba. *BP* 672,400

Trisazo dyes are made by treating an aminodisazo dye of the type a pyrazolone→*p*-phenylenediaminesulphonic acid→aniline (or a simple derivative, e.g. *m*-toluidine) with *m*- or *p*-nitrobenzoyl chloride, reducing the nitro group so introduced to NH$_2$, diazotising, and coupling with a 1-aminophenyl-3-methyl(or carboxy)-5-pyrazolone. The products dye cellulose fibres, and since they contain an NH$_2$ group, they can be diazotised and developed on the fibre, e.g. with β-naphthol. Thus, *p*-phenylenediaminesulphonic acid is treated with 1 mol. of HNO$_2$, so that diazotisation takes place only on the NH$_2$ *meta* to the SO$_3$H, and is coupled with 3-methyl-1-*p*-sulphophenyl-5-pyrazolone. The monoazo dye so formed is diazotised and coupled with *N*-methylaniline-*o*-sulphonic acid. After hydrolysis of the *N*-sulphomethyl group, the NH$_2$ is acylated with *p*-nitrobenzoyl chloride. The NO$_2$ group is reduced to NH$_2$ with Na$_2$S, and the aminobenzoylaminodisazo compound is diazotised and coupled with 1-*m*-aminophenyl-3-methyl-5-pyrazolone. The product—



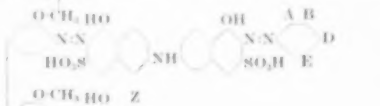
dyes cotton yellow-orange, becoming redder on diazotisation and development with β-naphthol or 1-phenyl-3-methyl-5-pyrazolone. E. S.

**Light-fast Blue Azoic Pigment.** American Cyanamid Co. *USP* 2,573,851

The pigment dianisidine (2:2-hydroxy-3-naphtho-*o*-phenetidide)$_2$ has high fastness to light if coupling is effected in presence of a cationic surface-active agent, preferably the reaction product of an octadecylguanidine salt with ca. 6 mol. of ethylene oxide. The product appears to be identical with that produced from less light-fast forms of the pigment by heat treatment at ~100° C. as described in *USP* 2,517,924 (see J.S.D.C., **67**, 201 (May 1951)). Thus, all parts being by weight, 2-hydroxy-3-naphtho-*o*-phenetidide (173) is dissolved in water (695) and NaOH (39). Sodium acetate crystals (100) dissolved in water (500) are added, and then more water (5000) and ice to bring to 0° C. A solution in glacial acetic acid (100) of the reaction product (34) of octadecylguanidine carbonate with 6 mol. of ethylene oxide, at 0° C., is added rapidly with good stirring to the coupling component solution. The suspension so produced is added to a tetrazo solution prepared from dianisidine (65·5). Development of the desired crystalline structure is brought about by heating to 90° C. E. S.

**Blue Copper-complex Trisazo Direct Cotton Dyes.** S. *BP* 673,696

Bright blue direct cotton dyes are made by treating trisazo compounds—



(A = OH, COOH, or O·CH$_3$; B = H, NO$_2$, Hal, Alk, or SO$_3$H; D = H, NO$_2$, or SO$_3$H; E = H, Hal, O·CH$_3$, NO$_2$, Alk, SO$_3$H, SO$_2$·NH$_2$, SO$_2$·NH·Alk, or SO$_2$·NH·C$_6$H$_5$; one X = SO$_3$H and the other X = H; Y and Z = H or SO$_3$H) with a demethoxylating copper-yielding agent. Thus, tetrazotised *o*-dianisidine is coupled first with 1 mol. of 1-naphthol-3:6:8-trisulphonic acid, and then with 1 mol. of 5:5′-dihydroxy-2:2′-dinaphthylamine-7:7′-disulphonic acid. The disazo compound so formed is coupled in

presence of 5–10% by vol. of pyridine with 1 mol. of diazotised 2-amino-4-chloro-5-nitrophenol. Treatment of the triazo compound with an ammoniacal solution of a copper salt gives a bright blue direct cotton dye. E. S.

**Disperse Dyes containing Sulphonyl Fluoride Groups.** American Cyanamid Co. *USP* 2,576,037

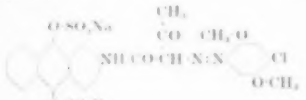
Aminomonazo compounds $Ar^1.N:N.Ar^2.NR^1R^2$ ($Ar^1$ = aryl of benzene series; $Ar^2$ = arylene of benzene or naphthalene series; $R^1$ and $R^2$ = H, alkyl, aralkyl, β-hydroxyalkyl, β-alkoxyalkyl, or β′-alkoxy-β-alkoxyalkyl) containing at least one $-SO_2F$ group are disperse dyes for acetate rayon and vinyl halide-vinyl acetate copolymers. Thus, 2-chloro-4-nitroaniline → 3-amino-4-methylbenzenesulphonyl fluoride is yellow, and aniline-*p*-sulphonyl fluoride → *NN*-bis-β-hydroxyethylaniline is orange. E. S.

**Metal-complex Polyazo Dyes for Leather.** Basf. *BP* 673,791

Brown and grey leather dyes are made by forming metal (e.g. Cr or Fe) complexes of polyazo compounds obtained by coupling 1 mol. of 2:6-bisdiazophenol-4-sulphonic acid with 2 mol. of a double-coupling azo component (e.g. resorcinol, 1-amino-5-naphthol) or 1 mol. each of a single-coupling and a double-coupling azo component, and combining the resulting disazo compound with 2 mol. of one or 1 mol. each of two different diazo compounds or with 0·5 mol. of 2:6-bisdiazophenol-4-sulphonic acid. This is made by tetrazotisation of 2:6-diaminochlorobenzene-4-sulphonic acid followed by treatment with $Na_2CO_3$ (see *BP* 16,811 (1901)). Thus, all parts being by weight, 2:6-diaminochlorobenzene-4-sulphonic acid (111) is dissolved in conc. HCl (240) and water (650), and ice (2000) added, followed by $NaNO_2$ (69). When tetrazotisation is complete, a soln. of $Na_2CO_3$ (160) in water (800) is slowly added, and the whole stirred for 30 min. and then made acid with conc. HCl, to give a solution of the required tetrazophenolsulphonic acid. This is coupled with a suspension of 1:8-diaminonaphthalene (182) in water (3000) containing glacial acetic acid (500), the disazo dye being isolated by adding $Na_2CO_3$ (500) and filtering off. It is then suspended in water (2000) and coupled with a diazo solution prepared from sulphanilic acid (173). The tetrakisazo compound so formed is isolated by addition of $Na_2CO_3$ (1000) and salt (1000), and boiled with $FeCl_3$ (162) and sodium acetate (123) in water (3500) for 3 hr., to yield the iron complex (420), which dyes leather brown. E. S.

**Sulphuric Esters of Leuco Anthraquinone Azo Vat Dyes.** Ciba. *BP* 673,226

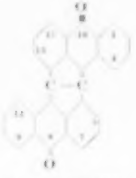
Sulphuric esters of leuco anthraquinone compounds containing one or two $NH_2$ groups attached directly, or through a bridge grouping, to β positions are converted into *N*-acylacetyl derivatives, which couple with diazo compounds to give soluble sulphuric esters of leuco vat dyes. The bridge grouping may be e.g. $-C_6H_4-$, $-CO.NH.C_6H_4-$, $-SO_2.C_6H_4-$, etc. If only one *N*-acylacetyl is present, the diazo compounds used are derived from amines free from solubilising groups, but if the molecule contains two *N*-acylacetyl groups, diazo compounds derived from amines like 2-aminoanisole-4-sulphonic acid are preferred, in order to confer sufficient solubility on the product. Thus, β-acetylaminoanthraquinone is treated with chlorosulphonic acid, iron powder, and pyridine to produce the leuco sulphuric ester, and the acetyl group saponified with aq. NaOH, giving the disodium salt of the sulphuric ester of *leuco*-β-aminoanthraquinone. Treatment with diketen then gives the *N*-acetoacetyl derivative, which couples with diazotised 4-chloro-2:5-dimethoxyaniline to give the azo compound—



Printed on cotton and developed with dil. nitrous acid, it gives pure yellows. E. S.

**Acedianthrone Derivatives—Vat Dyes.** ICI. *BP* 672,901

The halogeno (or amino) derivatives of acedianthrone—



prepared as described in *BP* 410,552 and 453,853 (*J.S.D.C.*, **50**, 331 (1934)) are condensed with amines (or halogen derivatives) of the benzene or naphthalene series, to produce non-tendering brown vat dyes with good printing properties. Thus, the aminoacedianthrone made by nitrating acedianthrone in 98% $H_2SO_4$ at 0° C., reducing with $Na_2S_2O_4$, and finally purifying by precipitating from 82% $H_2SO_4$, is heated at 207–210° C. for 8 hr. with *p*-bromotoluene, fused potassium acetate, and $Cu_2Cl_2$ in nitrobenzene.

*BP* 672,905

Aminoacedianthrone prepared as described above is acylated with 1-nitroanthraquinone-2-carboxylic chloride in nitrobenzene to give a brown vat dye with good printing properties. The dye produced by replacing the $NO_2$ with $NH_2$ has similar hue and properties.

*BP* 672,906

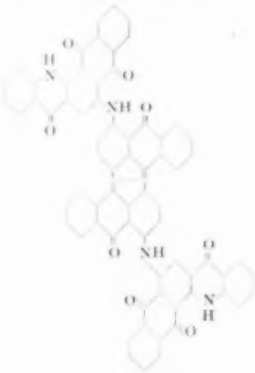
Two mol. of aminoacedianthrone are condensed with one mol. of 4:10-dihalogenoanthanthrone in naphthalene at 215–220° C. for 30 hr. in presence of $K_2CO_3$ and Cu salts to give olive-brown vat dyes of good printing properties.

*BP* 672,907

Equimol. proportions of aminoacedianthrone and the acylating derivative of a dicarboxylic acid, e.g. terephthaloyl chloride, are condensed in nitrobenzene containing pyridine at 100° C. The product is then further condensed with 1 mol. of a vattable amine, e.g. 1-aminoanthraquinone, to give brown vat dyes with properties similar to those previously described.

*BP* 672,908

7:15-Dichloroacedianthrone, obtained by treating the condensation product of 1-chloro-9-anthrone (reduction of 1-chloroanthraquinone) and glyoxal with acetic anhydride and $H_2SO_4$ in nitrobenzene (*BP* 551,622: *J.S.D.C.*, **59**, 155 (1943)), is heated at 215–220° C. with 3-amino-1:2-phthaloylacridone (*BP* 587,006: *J.S.D.C.*, **64**, 199 (1948)) in naphthalene containing $Na_2CO_3$ and Cu salts to produce the brown vat dye—



R. K. F.

**Sulphurised Tetracene (Naphthacene) Derivatives—Water-soluble Dyes.** Fran. *BP* 671,814

Water-soluble dyes for cellulosic fibres and silk, which are aftertreated to give greens fast to light and washing, are prepared by oxidising in acid medium the green pigment obtained by the action of sulphur chloride on tetracene—

Thus, sulphurised tetracene is stirred for 3 days at 15–30° C. in 45% $H_2SO_4$ containing $PbO_2$. The resulting yellow product is heated at 50–60° C. in aq. soln. to give the stable brown sulphate, which is applied from an acetic acid bath containing Glauber's salt. Aftertreatment with hot aq. alkali with or without $Na_2S_2O_4$ reproduces the green colour of the original sulphurised tetracene by hydrolysis. R. K. F.

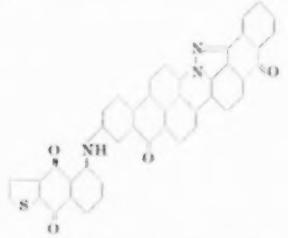
**Yellow Disperse Dyes from 4:6-Dihydroxypyrimidines.** Eastman Kodak Co. *USP* 2,578,280

Diethyl malonate condenses with suitable acylamidines to give 4:6-dihydroxypyrimidines—

(R = H, lower alkyl, monohydroxyalkyl of 2 or 3 C, or alkoxyalkyl of 3 or 4 C), which couple in position 5 with diazo compounds free from sulpho or carboxy groups to give yellow disperse dyes for cellulose acetate, etc. Thus, all parts being by weight, acetamidine hydrochloride (94·5) is added to an ice-cold solution of sodium ethoxide obtained by dissolving sodium (69) in ethanol (790). After filtering from the NaCl formed, diethyl malonate (160) is added. The solid which separates after standing for 24 hr. at room temperature is removed, dissolved in water, and precipitated with HCl; it is 4:6-dihydroxy-2-methylpyrimidine. It couples with diazotised o-phenetidine to give a greenish-yellow acetate rayon dye. E. S.

**Thiophanthraquinone Benzanthrone Pyrazoloanthrone Derivatives Vat Dyes.** DuP. *USP* 2,559,676

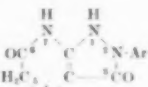
Grey vat dyes are produced by condensing mono- or di-halogenobenzanthrones with 1 mol. of an alkali salt of pyrazoloanthrone, further condensing the product with 1 or 2 mol. of 5- or 8-aminothiophanthraquinone, and finally cyclising by fusing with caustic alkali. Thus, the dye—



is prepared by refluxing pyrazoloanthrone, 3,9-dibromobenzanthrone, and $K_2CO_3$ in nitrobenzene for 4 hr. 5-Aminothiophanthraquinone with $CuCO_3$ and fused sodium acetate is then added, and refluxing continued for 20 hr. After being separated, the dry product is fused with KOH and ethanol at 95–100° C. for 6 hr. R. K. F.

**Pyrazolopyridine Derivatives.** ICI. *BP* 670,746

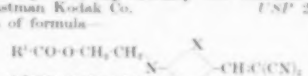
Compounds useful for making azo and styryl dyes, and as colour formers in colour photography, have the formula—



They are made by condensing a 3-amino-1-aryl-5-pyrazolone with a dialkyl malonate in presence of an alkali-metal alkoxide. Thus, 3-amino-1-phenyl-5-pyrazolone is refluxed with diethyl malonate in an alcoholic solution of Na for 20 hr. The product is separated by distilling off the alcohol and neutralising with acetic acid. R. K. F.

**Methin Dyes having Affinity for Acetate Rayon.** Eastman Kodak Co. *USP* 2,583,551

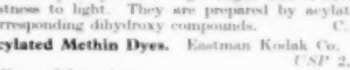
Dyes of formula—



($R^1$ and $R^2$ = $CH_3$, $C_2H_5$, $C_3H_7$, $CH_3{\cdot}O{\cdot}CH_2$, or $CH_3CH_2{\cdot}O{\cdot}CH_2$; X = H or $CH_3$) are greenish-yellow acetate rayon dyes fast to gas fumes and of exceptional fastness to light. They are prepared by acylating the corresponding dihydroxy compounds. C. O. C.

**Acylated Methin Dyes.** Eastman Kodak Co. *USP* 2,583,614

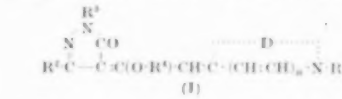
Dyes of formula—



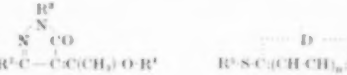
($R^1$ = $CH_3$, $C_2H_5$, $C_3H_7$, $CH_3{\cdot}O{\cdot}CH_2$, or $CH_3CH_2{\cdot}O{\cdot}CH_2$; $R^2$ = Alk of 1–3 C; $R^3$ = Alk of 1–4 C or $R^3{\cdot}O{\cdot}CH_2CH_2$; $R^4$ = Alk of 1–2 C; X = H or $CH_3$; when X = methyl $R^2$ may also be $R^4CO{\cdot}O{\cdot}CH_2CH_2$) give greenish yellows on acetate rayon which are fast to gas fumes and of exceptional fastness to light, and have good affinity for the fibre and good sublimation properties. Where X = $CH_3$ they absorb at a longer wavelength than when X = H and so are more orange-yellow. C. O. C.

**Photographic Sensitising Dyes.** Ilford. *BP* 672,291

Dyes of formula (I) ($R^1$ = Alk, aralkyl, or Ar; $R^2$ and $R^3$ = H, Alk, aralkyl, Ar, or heterocyclic; $R^4$ = Alk or aralkyl; n = 0 or 1; D = atoms to complete a 5- or 6-membered heterocyclic nucleus) are obtained by treating a compound of formula (II) with one of formula (III) ($R^5$ = Alk, aralkyl, or Ar; Y = an acid radical).



(I)

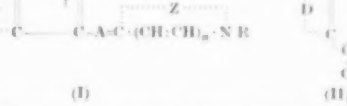


(II) (III)

C. O. C.

**Methin Dyes and Optical Bleaching Agents containing Coumarin Nuclei.** Ilford. *BP* 672,741

Dyes of formula (I) (A = CH, CH:CH·CH, or CH:C(S·Alk)·CH; D = atoms to complete a benzene ring; n = 0 or 1; Z = atoms to complete a 5- or 6-membered



(I) (II)

heterocyclic ring; R = Alk or aralkyl) are obtained by condensing an intermediate of formula II with a suitable compound. Dyes of various hues are obtainable—thus methin[2-(3-methyl-5-methylthio-1:3:4-dihydrothiodiazole)][4-(3-cyanocoumarin)] is orange, while trimethin[2-(1:3:3-trimethyldihydroindole)][4-(3-cyano-7-hydroxycoumarin)] is purple. 3-Cyano-4-methyl-7-hydroxycoumarin is a colourless product having strong bluish fluorescence, and is useful as an optical bleaching agent. C. O. C.

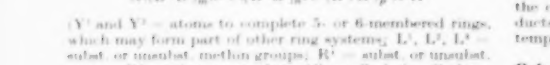
**Polymethin Dyes.** Gevaert. *BP* 673,061

Dyes of formula—

(Y¹ and Y² = atoms to complete 5- or 6-membered rings, which may form part of other ring systems; L¹, L², L³ = substd. or unsubst. methin groups; R¹ = substd. or unsubst. ammo; R² = substd. or unsubst. Alk, aralkyl, Ar, alkylene, or arylene; $m$ and $p$ = 0 or 1; $n$ = 1 or 2) or their *cyclo*ammonium salts have photosensitising properties. They are made by treating a cyanine dye intermediate with an $\omega$-acylazole. C. O. C.

**Symmetrical Tetranuclear Dyes from Bisthiazoles.** General Aniline. *USP* 2,579,432

Dyes of general formula—



(As = same CH, $(CH{\cdot}CH)_n{\cdot}CR^2{\cdot}(CH{\cdot}CH)_p$, or $CH_2(CH{\cdot}CH_2)_n{\cdot}CR^2{\cdot}(CH{\cdot}CH_2)_p{\cdot}CH_2$; $R^1$ = Alk or aralkyl; $R^2$ and $R^3$ = H or Alk, $R^2$ being H only when $n$ = 1; $n$ = 0 or 1; X = anion; Z = atoms to complete a 5- or 6-membered heterocyclic nucleus) are non-migrating photographic sensitisers which are unaffected by the presence of colour components. C. O. C.

**Pigments from Acid or Basic Dyes.** National Lead Co. *BP* 672,922

Intensely coloured, insoluble, non-bleeding pigments are obtained by mixing an aqueous solution of an acid dye with an aqueous solution of a water-soluble zirconium salt.

*BP* 672,923

Insoluble pigments of high tinctorial strength, soft texture, and brilliant hue, particularly suitable for use in printing inks, are obtained by mixing an aqueous solution of a basic dye with a negatively charged aqueous suspension of hydrous zirconia or hydrous zirconium phosphate, which suspension is produced by adding either an alkali or an alkaline phosphate to a solution of a Zr salt and then bringing it to pH 5. C. O. C.

**Carbon Black.** Columbian Carbon Co. *BP* 673,400

Modification of *BP* 667,329 (*J.S.D.C.*, **68**, 192 (May 1952)), furnace black having a fully oxidised surface, intense blackness, and markedly increased oil and iodine absorption characteristics being obtained if the treatment is carried on beyond the point of complete oxidation of the carbon surfaces.

*BP* 673,401

Furnace black treated by the above method so as to obtain the maximum colour value on the ABC colour scale has its iodine value much increased by heating it to 1800–2000° F. in a non-oxidising atmosphere.

*BP* 673,776

A method of making furnace black which gives a higher yield than hitherto possible. C. O. C.

**Carbon Black.** J. M. Huber Corpn. *BP* 672,074

A method of producing furnace black in which the time the pigment is at > 800° C. is much reduced.

*BP* 673,155

Method of making furnace black having the same particle size as channel black. C. O. C.

**Caramel.** Union Starch & Refining Co. *USP* 2,582,261

Caramel of high stability to acid, which does not thicken on ageing and gives brilliantly clear solutions, is prepared by hydrolysing starch and similar carbohydrates, heating for 15–20 min. at pH 0·2–4·0 and 200–250° F., adding ammonia to bring to pH 3·0–7·5, and caramelising while maintaining at pH > 2·0. C. O. C.

**Titanium Dioxide.** New Jersey Zinc Co. *BP* 671,728–9

Titanium dioxide of high pigment quality can be produced from the titaniferous slags obtained in the smelting of Fe–Ti ores by suitable oxidation of the titanium content of such slags having a valency < 4. C. O. C.

**Titanium Dioxide.** Säurefabrik Schweizerhall. *BP* 673,782

Modification of *BP* 661,685, whereby the rutile content of the pigment is increased to at least 40–60%. C. O. C.

**White Inorganic Oxide Pigments from Volatile Chlorides.** Säurefabrik Schweizerhall. *BP* 672,753

White inorganic oxide pigments, e.g. $TiO_2$, $ZrO_2$, or $SiO_2$, produced by decomposing volatile chlorides at high temperatures with oxygen-containing gases, are obtained free from iron, and so insensitive to light, if those parts of the chamber which are exposed to the hot reaction products are made from a ceramic which is refractory at the temperatures used and has an iron content of < 0·1%. C. O. C.

**Colour-shifting Agents for Zinc Oxide Pigments.** F. G. Smith. *USP* 2,579,020

Solid solutions of a coloured pigment in a white pigment have their colour altered by addition of a "colour shifting agent"; e.g. hexagonal ZnO containing 1% by wt. of CoO and 0·5% of MnO is heated to 1200° C. and 20% of MgO added, which changes the hue from green to blue-green. C. O. C.

Phthalocyanine Lubricating Greases (III p. 313).
Reduction Properties of Vat Dyes (VIII p. 325).
Use of Sulphamic Acid Derivatives in the Application of Oxidation Blacks (IX p. 326).
Photodichroism of Dye–Gelatin Films. III—Theoretical Consideration of the Photodichroism–Time Relation. IV—Dispersion of Photodichroism of Dye–Gelatin Films (IX p. 326).
Relaxation Phenomena in Photodichroism of Organic Dye–Gelatin Film (IX p. 327).
Electric Dichroism of Dye–Gelatin Films. III—Theoretical Consideration (IX p. 327).
Acylated Aminoacedianthrones—Brown Vat Dyes for Printing (IX p. 327).
Yellow Styryl Dyes as Colour Couplers in Automatic Masking Processes (IX p. 327).

## V—PAINTS; ENAMELS; INKS

**Protective Action of Paints.** J. E. O. Mayne. *Research*, **5**, 278–283 (June 1952).

Review of present knowledge. Corrosion may be inhibited by stopping either the cathodic or the anodic reaction or by inserting a high electrolytic resistance between the cathodic and anodic areas. Paint films are so permeable to water and oxygen that they cannot inhibit the cathodic reaction, and only when they contain certain pigments can the anodic reaction be suppressed. In general, paint films inhibit by virtue of their high electrolytic resistance. 24 references. C. O. C.

**Anticorrosion Properties of Aluminohemicellulose.** A. P. Antykov. *J. Appl. Chem. U.S.S.R.*, **25**, 39–45 (Jan. 1952).

Aluminohemicellulose (AHC), a material that is precipitated in a crude form (10–18% of AHC) by the addition of sodium aluminate to used mercerising liquor from viscose manufacture, is proposed for use as a corrosion inhibitor. It is more effective than known inhibitors for preventing the corrosion of iron by $H_2SO_4$ solutions; thus, addition in the crude form of 0·05% of AHC to a 26% soln. of $H_2SO_4$ reduces the rate of dissolution of iron from 10·8 to 0·067 g./sq.m. per hr. AHC is of some value for the protection of iron in solutions of $H_3PO_4$, but is of no value in solutions of HCl and $HNO_3$. The inhibiting action against $H_2SO_4$ and air is greatly reduced when the iron surface is initially rusty. Addition of 2–5% of refined AHC to protective paints greatly increases the protection afforded against corrosion by acid and by air. A. E. S.

**Pigment Dyes and Litho Inks—Significance of pH Measurement.** J. Keaton. *J. Oil & Col. Chem. Assocn.*, **34**, 586–591 (Dec. 1951).

The occasional tendency of the "fountain" soln. to "break back" into the ink during lithographic printing is related to the pH of aqueous extracts of the pigment. Pigments from various sources gave extracts with pH variations from 3·0 to 9·2, and those with high pH (above ca. 8·0) gave trouble in printing. Prior treatment with dil. benzoic acid in one case remedied the fault. A. J.

PATENTS

**Black Printing Inks.** J. M. Huber Corpn. *USP* 2,580,205

Inks consisting of carbon black and an oil-soluble dye in a liquid vehicle containing water-immiscible liquid, e.g.

mineral or vegetable oil, do not "burn out", i.e. suffer progressive decrease in colouring effect on ageing, if a small amount of an oil-soluble zinc salt, preferably zinc naphthenate, is added to them. C. O. C.

**Water-emulsion Paints.** Dow Chemical Co. *BP* 672,290

Paints which do not putrefy and which yield films which are resistant to abrasion immediately after drying consist of aqueous colloidal dispersions of a pigment and a mixture of polymerisable unsaturated organic compounds including at least 15 mole % of a monovinyl aromatic hydrocarbon and 40–60 mole % of 1:3-butadiene. C. O. C.

**Solvent Resin Type of Printing Inks.** IC. *USP* 2,579,836

Inks which dry extremely rapidly when heated consist of pigment dispersed in petroleum hydrocarbon solutions of modified Utah coal resins (described in *USP* 2,568,591), the solvents being those that dry only very slowly at 20° c. but evaporate rapidly at 150° c. C. O. C.

**Dispersing Pigments in Film-forming Material.** DuP. *USP* 2,581,414

Pigments are dispersed in film-forming material and/or their particle size is decreased by agitating them in suitable apparatus with 20–40 mesh sand (A.S.T.M. Specification E-11 for Sieves) in presence of a film-forming dispersing material. C. O. C.

**Surface-coating Compositions containing Ethers of Catechol-type Tanning Agents.** Standard Dye-wood Co. *USP* 2,582,500

Ethers of, or the hydroxymethyl or polymethylene derivatives of the ethers of, natural polyhydroxy phenolic tanning materials, e.g. cutch or quebracho extract, obtained e.g. by the sequential etherification of the tanning material with firstly monochloroacetic acid and then an aralkyl halide, when mixed with alcohol-soluble proteins, e.g. zein, are quick-drying coating compositions which yield clear and highly lustrous films. C. O. C.

**Coating Compositions.** Harvel Research Corpn. *USP* 2,584,657

A solution of > 1 part of trioxan and 1 part of a solid film-forming material yields coatings of various macro-crystalline configurations, e.g. needle-like, fish-scale, fan-shape, etc., which may be dull, glossy, mirror-like, "pearlescent", etc., these effects being imparted to the coating by the crystallisation in it of the trioxan. C. O. C.

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Hydro-polyalkoxysilyl Addition Products of Rubber (III p. 314).
Daylight-fluorescent Pigments and Coating Compositions (IX p. 327).
Polyester Copolymers (XIII p. 332).

## VI—FIBRES; YARNS; FABRICS

**Deformation Process of Cellulose Gels and X-Ray Measurements of Orientation.** W. Kast. *Kolloid-Z.*, **125**, 45–51 (Jan. 1952).

The paper summarises and discusses prevailing theories on the degree of orientation of fibre crystallites as shown by analysis of the distribution of intensity along the arcs of their X-ray diffraction photographs. Measurements from such photographs of different cellulosic materials at various degrees of extension are given, which indicate that the crystallites do not have the form of long rodlets which orient themselves along the fibre axis, as is usually assumed, but are more probably sheet-like in form, with the normal to the plane becoming perpendicular to the axis as the fibre is stretched. The narrow edge of the sheet does not similarly orient itself, except in cellulose gels capable of a high degree of swelling, spun from baths of low concentration or of not too high a degree of polymerisation. Thus, this "sheet-effect" (*Blattchen-Effekt*) comes into greater prominence as the cross-linking in the lattice increases, a deduction which is also supported by data showing the increase in the extension at break as the degree of such orientation decreases. More rapid stretching tends to increase the "sheet-effect", but higher temperatures of the water in the spinning-bath oppose this. The experimental results are considered to be evidence that some of the bonds holding the structure together must be labile before orientation in both directions is possible. L. P.

**Mechanism of the Ripening of Viscose.** A. Matthes. *Faserforsch. und Textiltech.*, **3**, 127–141 (April 1952).

An account is given of hitherto unpublished work done in the I.G. laboratories in 1930–1931 in which the method developed by the author and others for determining the ripeness ($\gamma$ number) of viscose by precipitation with diethylchloroacetamide is applied to the study of the ripening process. Diagrams are given showing the effects on the ripening process of the concn. of free NaOH, of the concn. of unesterified hydroxyls, present either in the cellulose itself or in added alcoholic substances ($CS_2$-acceptors), and of the presence of atmospheric oxygen, sulphides, sulphites, $CS_2$ by-products, or polyhydroxy compounds. The formation and ripening of xylan xanthate are discussed in connection with the effect of the xanthation of the 2- and 3-OH groups of cellulose on the ripening process. The relation between the ammonium sulphate coagulation number and the $\gamma$ number is examined. Ripening is fully accounted for by a xanthate hydrolysis mechanism only when the viscose is prepared with the exclusion of oxygen or in presence of a sulphite. The rate of ripening is greatly increased by the atmospheric oxygen introduced during sulphidation; sodium sulphide, which is present in low concn., being formed constantly but transiently in the course of a sequence of reactions, acts as a catalyst in this reaction. All three cellulose hydroxyls may be xanthated, but the 2- and 3-xanthates are much less stable than the 6-xanthate—this is in accord with the instability of xylan viscose and the acceleration of ripening caused by additions of 1:2 polyhydric alcohols to viscose. The instability of the 2- and 3-xanthates accounts for the abnormally high initial ripening rate of viscose. Polyhydric alcohols act as carriers of $CS_2$ to the alkali phase, and, in their presence, the $Na_2S$ concn. is increased, and the uptake of oxygen and the ripening process are accelerated. During ripening, the ratio of the coagulation number to the $\gamma$ number falls rapidly at first and then remains almost constant. This is attributed to a redistribution of the groups formed in the initial attack, leading to a dynamic equilibrium in which an even distribution of xanthate groups within the cellulose is attained. A microtechnique for determining $\gamma$ numbers is described. A. E. S.

**Nitration of Cellulose—Accessibility to Nitrating Agents.** J. Chédin. *Kolloid-Z.*, **125**, 65–72 (Feb. 1952).

Aqueous nitric acid is regarded as an equilibrium mixture of the ions and the undissociated acid in the form of the trihydrate, monohydrate, and anhydrous molecules. Only the last-named are the effective nitrating species, and their calculated concentration plotted against the degree of nitration of cellulose at different dilutions agrees well with that of a dynamic equilibrium whose constant $K = 0{\cdot}3$. Although acetyl nitrate ($CH_3COONO_2$) in acetic anhydride or carbon tetrachloride can nitrate liquid alcohols and even solid pentaerythritol, it is found to nitrate dry cellulose only as far as a nitrogen content of 1·6–2·0% after 4–5 hr. at room temperature. If the cellulose is pretreated with acetic acid, however, and this swelling agent subsequently removed by soaking in acetic anhydride, it can then be nitrated with a 22% solution of acetyl nitrate in carbon tetrachloride to an N content of 12·2%, in 4 hr. at 10° c. Similarly, solutions of nitric acid in acetic anhydride (mole ratio 1 : 4) give dry cellulose an N content of only 0·35% after 3 hr. at 100 c., whereas pre-swollen cellulose will take up as much as 13·6% in 5 hr. at 10° c. or in 20 hr. at 0° c. Cellulose swollen with water and then dried by means of 95% alcohol followed by absolute alcohol, which is then removed by acetic anhydride, can also be nitrated to 10% N content by the same reagents. The function of sulphuric acid in the usual nitrating mixture is thus to swell the fibre to permit penetration by the reagent and to make the OH groups in the cellulose more reactive by breaking the hydrogen bonds between them. L. P.

**Structure of Alginic Acid—II.** S. K. Chanda, E. L. Hirst, E. G. V. Percival, and A. G. Ross. *J.C.S.*, 1833–1837 (May 1952).

Experimental data are submitted which confirm the view that the main structural feature of the alginic acid molecule is a chain of 1:4-linked $\beta$-D-mannuronic acid residues, the chain length of the sample of alginic acid used being ca. 100. H. H. H.

**The Reaction between Wool and Nickelammonium Hydroxide. I The Adsorption of Nickel by Wool from Solutions of Nickelammonium Hydroxide.** J. W. Bell and C. S. Whewell. *J.S.D.C.*, **68**, 299–305 (Aug. 1952).

**Studies on the Microbiological Degradation of Wool. I Sulphur Metabolism.** W. H. Stahl, B. McQue, G. R. Mandels, and R. G. H. Siu. *Office of the Q.M. General, Biochemical Series Report* 2* (Oct. 1948). Pp. 27.

**II Digestion of Normal and Modified Fibrillar Proteins. III Further Sulphur Metabolism Studies. IV Nitrogen Metabolism.** Idem. *Ibid.*, *Report* 3* (Aug. 1949). Pp. 67

**I.** A study of the sulphur metabolism of *Microsporum gypseum* as concerns fungal degradation of wool.

**II IV.** The susceptibility to attack by the fungus *Microsporum gypseum* of various forms of keratin including mohair, horse hair, and wool, before and after various treatments, has been studied. C. O. C.

*Available from T.I.D.C., D.S.I.R., Cunard Building, 15 Regent Street, London S.W.1.

**Effect of Ammonium and Potassium Salts on the Stability and Viscosity of Solutions of Rennet Casein.** N. M. Turkevich. *J. Appl. Chem. U.S.S.R.*, **25**, 104–108 (Jan. 1952).

It is considered that rennet casein should yield a better textile fibre than acid casein, if technical difficulties associated with the instability of its soln. and the low rate of filtering can be overcome. It is found that casein swollen in presence of diammonium hydrogen citrate, ammonium hydrogen fluoride, ammonium hydrogen tartrate, ammonium oxalate, or potassium hydrogen oxalate gives an alkaline soln. that filters much more readily and shows a slower rise in viscosity during ripening. A. E. S.

**Water Sensitivity of Glass Fibre.** W. Boheth. *Faserforsch. und Textiltech.*, **3**, 142–146 (April 1952).

Treatment of alkali glass fibres with water leads to a permanent reduction in the tensile strength, the effect being particularly notable in yarn and fabric. Thus, unprocessed fibres of current production are found to have a retained strength, measured dry, of 71%, after boiling for 1 hr. in water. A short treatment is generally sufficient to produce the max. loss; further treatment may lead to a slight recovery in strength. The loss in strength is often aggravated by the presence of acids or anion-active auxiliary agents, while alkalis and cation-active agents have the reverse effect. Thus, the retained dry strength of a glass fibre ribbon after a 1-hr. treatment at 20° C. followed by drying at 60° C. is 93% for water, 47% for 0·5 N HCl, and 104% for 2 N NaOH. A. E. S.

PATENTS

**Refining Agave and Manila Hemp Films.** J. Rinse and W. Dorst. *BP* 673,671

Binding or encrusting substances are removed from between the fibres of agave or Manila hemp, and the flexibility is improved, by treating at not > 60° C. with a solution of alkali metal hydroxide (< 15%, calc. as NaOH) containing Al and/or Zn oxide or hydroxide. Typical concentrations are 3–10% NaOH, 2–6% $Al_2O_3$, and 1–3% ZnO. J. W. B.

**Spun Yarns of High-tenacity Regenerated Cellulose.** Celanese Corpn. of America. *USP* 2,581,566

A tow of continuous filaments of an organic ester of cellulose is plasticised or softened and then stretched. The filaments are then deplasticised, and the tow is converted to a sliver by breaker-drafting. Roving formed from this sliver is then saponified, washed, dried, and spun. C. O. C.

**Cellulose Compounds soluble in Dilute Acid and Alkali.** Courtaulds. *BP* 671,383

Water insoluble, alkali-soluble, and acid-soluble cellulosic material is made by impregnating cellulose with an aq. soln. containing not < 20% by wt. of $H_2SO_4$, not < 15% of cyanamide, and 0·5–8% of free orthophosphoric acid or the equivalent amount of water-sol. orthophosphate, drying the impregnated material, and baking at not < 110° C. In one example a skein of regenerated cellulose yarn (3 g.), washed but not dried, is impregnated for 2–3 min. in an aq. soln. containing 15 N $H_2SO_4$ (13 ml.), $(NH_4)_2SO_4$ (12), $NH_4H_2PO_4$ (0·5), and cyanamide soln. (30–35%, 30 ml.). After hydroextraction the yarn is dried at 60° C., baked for 2·5 min. at 160° C., and washed in 30–40% aq. alcohol. The product dissolves in < 30 min. in approx. 0·01 N HCl and in 10 min. in 0·17% $Na_2CO_3$, and is thus suitable for carrier yarns. J. W. B.

**Cellulose Derivatives containing a Morpholine Group and having Affinity for Acid Dyes.** Celanese Corpn. of America. *USP* 2,579,873

Cellulose derivatives containing a morpholine group as a substituent are readily dyed with acid dyes. Dyed with acetate rayon dyes they have better fastness to gas fading than the unsubstituted material. C. O. C.

**Carrotting.** Frank H. Lee Co. *USP* 2,582,086

An aqueous solution containing a non-hydrolysing oxidising agent (3–5% by wt.), a volatile hydrolysing acid (1·0–4·5), and as catalyst phosphotungstic or phosphomolybdic acid (0·1–1·0), used as the carrot', results in a strong, high-quality felt being finally produced. C. O. C.

**Improving the Dyeing Properties of Fur boiled in Sulphuric Acid.** Hat Corpn. of America. *USP* 2,581,296

Fur which has been boiled in sulphuric acid is given improved felting properties and its affinity for dyes is increased by giving it a surface coating of a water-insoluble reactive nitrogen-base formaldehyde polymer before, during, or after carrotting. C. O. C.

**Artificial Protein Filaments.** Courtaulds. *BP* 673,676

High-tenacity protein threads are produced by denaturing the protein by subjecting it to the action of $Na_2S$, thioglycol, sodium thioglycollate, or $NaHSO_3$, extruding it into filaments, hardening if desired, and stretching at not < 70° C. J. W. B.

**Fibre- and Film-forming Copolymers of Dichlorodifluoroethylene and Ethylene.** DuP. *USP* 2,584,126

Dichlorodifluoroethylene–ethylene copolymers (95·19 : 5·81) have fibre- and film-forming properties. C. O. C.

**Polyamide-sulphones.** BrC. *BP* 670,177

Fibre-forming polyamide-sulphones are obtained by oxidising the corresponding polythioetheramides with hydrogen peroxide in a high concentration of a lower fatty acid. W. G. C.

**Polyacrylonitrile Filaments.** Vereinigte Glanzstoff-Fabriken. *BP* 673,491

Discoloration during spinning of a solution in a volatile solvent containing not < 85% acrylonitrile is avoided if throughout spinning the solution is kept out of contact with oxygen. C. O. C.

**Acrylonitrile Vinylpyridine Copolymers.** DuP. *BP* 670,268

The copolymers of acrylonitrile (98·90) and vinylpyridine (2–10) are fibre-forming and have good affinity for acid dyes.

*BP* 670,269

Copolymers containing 2–25% vinylpyridine, especially those containing > 10% vinylpyridine, which are not readily formed, can be made by heating at 30–100° C. an aqueous emulsion, of pH 7·10·5, of acrylonitrile, vinylpyridine, and a water-soluble persulphate catalyst. Copolymers containing 2–10% vinylpyridine have good water resistance and sufficient strength for fibre formation. These products have a good affinity for acid dyes. W. G. C.

**Acrylonitrile Polymer Compositions for Melt Spinning.** DuP. *USP* 2,580,393

Polymers, copolymers, or interpolymers containing not < 80% by wt. of acrylonitrile are readily melt-spun if they are dissolved in *N*-acetylmorpholine, *N*-acetylpyrrolidine, *NN'*-diacetyl-*NN'*-dimethylhydrazine, *NN'*-diacetyl-*NN'*-dimethylmethylenediamine, *NN'*-diacetyl-*NN'*-dimethylethylenediamine, or *NN'*-diacetylpiperazine. C. O. C.

**Wet Spinning of Acrylonitrile Polymers and Copolymers.** American Cyanamid Co. *USP* 672,775

Acrylonitrile polymers or copolymers in water-coagulable solution when extruded into an aqueous coagulant at not > 10° C. form filaments which may be oriented by stretching. C. O. C.

**Acrylonitrile Copolymers of Improved Dyeing Properties.** Koppers Co. *USP* 2,583,325–6

Copolymers of acrylonitrile, monoesters of itaconic acid, and if desired a diene of formula $CH_2{:}CR{\cdot}CR{:}CHR$ (R =

H or $CH_3$) have good affinity for many dyes, especially basic and acetate rayon dyes, owing to absence of cross-linking.

*USP* 2,583,327

Copolymers of acrylonitrile and an ethylene-αβ-dicarboxylic monoester of a cyanoalcohol of < 5 C have the same excellent dyeing properties as the above copolymers, and have better resistance to solvents and better tensile strength and other properties dependent on the high secondary bonding force of the acrylonitrile cyano groups. C. O. C.

**Polyethylene Terephthalate Bristles.** DuP.
*BP* 672,449

**Hardening Filaments.** Redding Manufacturing Co.
*BP* 672,669

Filaments of hardenable material, e.g. rubber latex, are discharged in liquid form into a narrow space enclosed by flat surfaces and containing a hardening liquid, e.g. glycerol, which flows through as a flat sheet and coagulates and carries forward the filaments. J. W. B.

**Fibrous Insoluble Alginates.** J. E. Hansen.
*BP* 672,896

Insoluble fibrous alginates, useful as fillers in the paper industry, are produced by treating alginic acid or an alkali-metal alginate with a conc. soln. of an alkaline-earth metal salt, e.g. a 20% soln. of $CaCl_2$, while it is being subjected to a mechanical process, e.g. milling. J. W. B.

Alleged Beckmann Rearrangement of Quinone Monoxime (IV p. 315).
Kinetics of the Decomposition of Solid Cotton Cellulose in a High-frequency Electromagnetic Field (XI p. 329).
Terephthalamide Derivatives (XIII p. 332).

## VII — DESIZING; SCOURING; CARBONISING; BLEACHING

**Requirements of a Detergent.** A. S. C. Lawrence. *Chem. and Ind.*, 183–184 (1 March 1952).

A brief discussion of some fundamental problems in connection with the mechanism of detergent action. W. K. R.

**Application of Ultrasonic Energy in Wool Scouring.** E. I. Garbinskaya, N. N. Dolgopolov, A. I. Matetsky, and E. L. Ruban. *Tekstil. prom.*, **12**, 10 (April 1952).

Laboratory experiments show that the scouring of wool in presence of ultrasonic waves is very effective. Neutral or only weakly alkaline solutions may be used, and the product is whiter, softer, and freer from fibre damage than wool scoured in the usual way in an alkaline soln. Ultrasonic waves are particularly effective for the disinfection of wool; they render both the wool and the effluent completely sterile, while having no deleterious effect on the fibre. A. E. S.

PATENTS

**Bleaching Wood Pulp.** Buffalo Electro-Chemical Co.
*BP* 671,962

Moist felted wood pulp containing substantial amounts of ligneous and other non-cellulosic materials and of not < 25% solids content is impregnated with an aq. peroxide as the sole bleaching agent. The solution has pH 9·5–11·5, and total alkalinity 0·35–1·1% by weight of $Na_2O$ equivalent based on bone-dry pulp. It comprises a peroxide or persalt which produces $H_2O_2$ in aqueous soln. and an alkaline salt including as an essential ingredient sodium silicate, trisodium phosphate, sodium pyrophosphate, or sodium tetraphosphate. The impregnated felted pulp is accumulated into a mass of substantial volume and relatively small area to inhibit drying out, and left for 5 hr. to several weeks. Maximum brightness is attained during the initial period, and the pH automatically lowered to at most 8 at the point of maximum brightness, which without further chemical addition to inhibit colour reversion is retained for at least several weeks. Alternatively the moist felted pulp may contain 35–50% solids and the peroxide may be applied at 15–30° C. In the attainment of maximum brightness the pH is automatically lowered to 6–8. S. V. S.

**Separating Vegetable Residues from Animal Fibres.** S. Carbonetto.
*BP* 672,911

Vegetable impurities, e.g. burrs, in animal fibres are treated with graphite or silver nitrate in such a way that only the vegetable material is coated. An electrolytic process then coats them with a film of iron, and subsequent passage through a high-frequency electric field causes them to be shaken out of the fibrous mass. J. W. B.

## VIII — DYEING

**High-temperature Dyeing of Textiles.** L. Duijvers. *Textiles*, **17**, 294–313 (May 1952); *Melliand Textilber.*, **33**, 525–531 (June 1952).

Experimental work on high-temp. dyeing of cotton with direct and vat dyes; wool with acid, acid milling, and chrome dyes; nylon with acid, disperse acetate, pre-metallised, direct, and vat dyes; Orlon with disperse acetate and acid dyes; Acrilan with disperse acetate, acid, direct, and premetallised dyes; and also unions. Details are given of the Steverlynck apparatus for dyeing with superheated steam under pressure. B. K.

**Developments in Research and Application of Direct Dyes.** J. Wegmann. *Textiles*, **17**, 275–287 (May 1952).

A discussion of published work on the theoretical aspects of the properties of direct dyes, including copperable dyes, with 29 references. B. K.

**Reduction Properties of Vat Dyes.** W. J. Marshall and R. H. Peters. *J.S.D.C.*, **68**, 289–299 (Aug. 1952).

**Relationship between the Chemical Constitution of certain Azoic Dyes and their Affinity for Acetate Rayon.** H. Wahl. *Textiles*, **17**, 288–294 (May 1952).

A series of experiments are described showing the effects of variation in coupling components, concn. of dye-bath, time of dyeing, and the addition of various dispersing agents on a number of azoic combinations applied to acetate rayon. Additional tests were also carried out with several combinations on Rhovyl at 75° C, and Terylene at 95° C, in the presence of soap and acetyl glycol or alcohol as solvent. B. K.

**Dyeing Turkey Red on Mixtures of Cotton and Viscose Staple.** J. B. Pugh. *Ion*, **11**, 322–326 (1951); *Chem. Abs.*, **46**, 4235 (10 May 1952).

Alizarin dyes cotton more intensely than viscose rayon, the converse being true of Naphtol AS. Cotton takes up rancid olive oil readily, but viscose does not, the reverse being the case with K or $NH_4$ ricinoleates or sulphoricinoleates or sulpho-oleates. Level dyeings of satisfactory fastness are obtained on cotton–viscose rayon mixtures by mordanting overnight in Al sulphoacetate (15–20 g./litre) at pH 5·2, rinsing with water of high temporary hardness to help fix the mordant, dyeing in a liquor (1 : 20–25) of hard water (180 mg. $CaCO_3$ per litre) containing 8–10% (on the weight of the fibres) of Alizarin Red extra 20% paste. The colour is finally developed by immersion in boiling water for 2 hr. or by steaming. Aftertreatment with Sn soap gives a beautiful yellowish dyeing. C. O. C.

**Dyeing of Vinylon. I — Swelling Method with Aqueous Phenol.** S. Hidaka and S. Suzuki. *J. Soc. Textile Cellulose Ind. (Japan)*, **7**, 435–436 (1951); *Chem. Abs.*, **46**, 4235 (10 May 1952).

Vinylon (formalised polyvinyl alcohol) swollen with 5% aq. phenol at room temp. and pH 6 for 30 min. was readily dyed with Nippon Sky Blue 5B, for which the untreated fibre has practically no affinity. C. O. C.

PATENTS

**Dyeing One Side of a Fabric a Different Colour from the Other Side.** Dan River Mills. *USP* 2,580,873

The fabric is dyed with a sulphuric ester of a leuco vat dye which oxidises on exposure to light, one side of the dyed fabric being exposed to light and the unoxidised dye then washed off the other side. This dyes one side of the fabric, which if already coloured has now a different colour on one side from the other. If an uncoloured fabric is being treated, then the process is repeated with a different dye, the side which is exposed to light and that from which the unoxidised dye is washed off being reversed. C. O. C.

**Coloured Glass Fibres.** Owens-Corning Fiberglas Corpn. *USP* 2,584,763

The material is treated with a salt of a metal whose

oxide colours glass and is then heated to drive off the non-metallic component of the salt. Thus glass is coloured brown by dipping in 4% aq. $FeCl_3$ and then heating for 3 min. at 600–700°F.; and a bluish purple is obtained by treatment with a 2% aq. dispersion of Ni naphthenate (made from a 70% soln. in Stoddard solvent) and heating for 2 sec. at 1100°F., or a greenish yellow by heating for 1 min. at 600°F. C. O. C.

**Fluorescent Materials.** R. C. Switzer. *BP* 672,762

Coloured effects of great intensity in daylight are obtained by using a diffusely reflecting backing sheet having dispersed on or in it a dye which reflects and fluoresces in the same colour, the dye being present in such dilution that it exhibits hyperintensity of colour in daylight, i.e. brightness greater than that given in daylight by reflection only by any dye or pigment of the same colour under the same conditions. Thus 6 oz. of white acetate rayon satin dyed for 2 min. at 180°F. in an aqueous bath containing 15% formic acid and 0·17% *m*-diethylaminophenolphthalein hydrochloride is a hyperintense cerise, and silk dyed for 2 min. at 150°F. in an aqueous bath containing 0·5% of the Na salt of 4-methyl-7-hydroxycoumarin is a hyperintense blue. C. O. C.

**Hair Dyes.** D. J. Donker. *BP* 673,489

A hair dye which imparts deep gloss, silkiness, and uniform coloration consists of 5–25% foho hennae, 10–50% of fatty alcohol sulphonate, and 0·5–10·0% of a basic dye containing 2–4 amino groups which may be substituted by lower alkyl groups, together with Na phosphate or other assistants. This dyes hair fast to washing but has the advantage that it is slowly removed by mechanical treatment, e.g. repeated brushing. C. O. C.

**Dyeing Oranges.** Franklin Research Co. *USP* 2,582,868

An oil-soluble dye dissolved in a non-ionic solvent capable of being diluted in water, e.g. FD&C Red 32 (3 parts by wt.), polyoxyethylene sorbitan monostearate (40·45), polyglycol *cyclo*pentanoate (40·45), and morpholine (4·1), is a colour concentrate for dyeing oranges. The fruit is immersed at a suitable temperature in a liquor obtained by diluting the concentrate with 20–200 times its volume of water. C. O. C.

Use of Sulphamic Acid Derivatives in the Application of Oxidation Blacks. (IX this page).
Dyeing of Leather. (XII p. 331).

## IX—PRINTING

**Neutralisation of Diazo Solutions with Chalk.** V. E. Rostovtsev, E. S. Makarenova, and V. V. Gromova. *Tekstil. prom.*, **12**, 25–26 (March 1952).

In agreement with Shagm (see *J.S.D.C.*, **67**, 289 (July 1951)), it is found that diazo solutions neutralised with chalk and then filtered are somewhat more stable than those neutralised with sodium acetate. This, however, is a result of the absence of buffer salts, which leads to a great increase in acidity as soon as decomposition sets in. The absence of buffer leads also to unsatisfactory conditions for coupling during printing and hence to a poor yield. Shagm's recipe is not to be recommended. A. E. S.

**Kyo-Kechi Ancient Japanese Method of Printing.** Anon. *Kuncha Textile Review*, **1**, (4), 3 (31 Jan. 1952).

The *Kyo-Kechi* method of printing originated in India, passed to Japan via China in the seventh century, and flourished in the eighth century. The fabric is folded in two, and is then fastened tightly between two thick wooden blocks on which the design has been engraved, one block being the mirror image of the other. These blocks have to be engraved with great accuracy, as it is essential that the raised portions on the one block meet those on the other perfectly. The two blocks form a closed chamber except for a feed hole, into which dye liquor is poured. The liquor is allowed to stay as long as necessary, it is then drained off through the feed-in groove, and the fabric is dried before the blocks are taken apart. This results in the patterns being produced in exactly the same position on each side of the fabric. Old fabrics can be found occasionally that have different designs on each side, and it is thought that this may have been effected by the simultaneous use of more than one set of blocks or of blocks twice as large as usual and bearing more than one design. Usually only one colour was used, but multicolour prints are not uncommon, generally in striped patterns; it is thought that in this case a single-colour print was made first, and the additional colours were then brushed on by hand.

The principle is now being revived by hand printers in Japan and in the making of *kasuri*, or intercross weaving, fabrics. A very small reproduction of a fabric known as *Kyo-Kechi*, listed as one of Japan's national treasures, which has been in the possession of *Shosoin* for thirteen centuries, is given. C. O. C.

**Orthophosphoric Acid in the Printing of Brentogen and Soledon Dyes.** A. G. H. Michie. *J.S.D.C.*, **68**, 257 (July 1952).

**Diazotype Printing Process.** L. van der Grinten. *Photographie J.*, **92 B**, 43–48 (March–April 1952).

A review of developments in diazotype printing since 1945. Negative diazotype processes date from 1884, but the positive processes have become of greatest importance, and are widely used for reproduction of line drawings. They are based on an invention by Green, Cross, and Bevan (1890), positive diazotype paper being first successfully marketed by Kalle & Co. in 1923 as Ozalid M. In spite of the need for powerful light sources, increasingly met by the use of mercury-vapour lamps, they are increasing in popularity because of the simplicity of their processing requirements.

Wood sulphite pulp is the preferred base, either directly impregnated with the light-sensitive solution, or preferably coated with a sensitised polymer layer, to improve definition and contrast. Transparent films of Cellophane or cellulose acetate sheet may also be used.

Two-component materials, for dry development with ammonia fumes, may contain a *p*-diazodialkylaniline with e.g. 2·3-dihydroxynaphthalene (I) or its 6-sulphonic acid (II) (for blues), monosubstituted resorcinol derivatives (for browns and yellows of good ultraviolet absorption, for intermediate prints), or the same with I and II (for blacks). *p*-Diazodiphenylamine and R acid are also used for blues.

One-component materials may contain e.g. *p*-diazoalkylanilines of higher coupling activity, or *p*-diazo-2:5-dialkoxyanilides, for coupling by aftertreatment in buffered developing liquids containing highly active coupling components, e.g. phloroglucinol, resorcinol, α- or β-naphthol, methylphenylpyrazolone, acetoacetanilide, at appropriate pH values, e.g. 6–7 or 9–10.

Acid stabilisers, e.g. tartaric, boric, or naphthalenetrisulphonic acid, are incorporated into the sensitising liquid.

Discoloration of white parts of prints, in either the light or the dark, due to deterioration of the decomposition products of the diazo compound and the coupling component, may be lessened by e.g. thiourea or thiosulphate, the latter used in developing solutions. Light fastness is not usually good, though this is of little importance, but *p*-diazodialkoxyanilides and 2-diazo-1-hydroxynaphthalene-5-sulphone acid give the best results.

Mercury-vapour lamps are especially suitable for exposure, because they have strong emission lines in the absorption region (3500–4500 A.) of the diazo compounds, and their size and shape are convenient for the construction of efficient printing machines. Intermediate prints can be made with lines of such high ultraviolet absorption that they give clearer copies than the original (e.g. a pencil tracing) and eradication on them may be easier than on the original.

A list of 20 general publications and 116 references are given. C. H. G.

**Use of Sulphamic Acid Derivatives in the Application of Oxidation Blacks.** C. Zuber and B. Jomain. *J.S.D.C.*, **68**, 241–248 (July 1952).

**Photodichroism of Dye–Gelatin Films. III—Theoretical Consideration of the Photodichroism–Time Relation.** D. Yamamoto. *J. Chem. Soc. Japan, Pure Chem. Sectn.*, **77**, 948–950 (1951); **IV—Dispersion of Photodichroism of Dye–Gelatin Films.** R. Iwaki and D. Yamamoto. *Ibid.*, 950–953; *Chem. Abs.*, **46**, 3859 (10 May 1952).

**III**—The results of theoretical consideration of photodichroism, especially of photodichroism–time relations, using the theory of anisotropic bleaching or discolouring, assuming two bleaching states of the dye molecules, agreed

qualtatively with previous work (cf. *A.S.D.C.*, **68**, 228–229 (June 1952)). There is, however, some disagreement with the work of Lewis *et al.* (*Chem. Abs.*, **36**, 343; **37**, 833, 3348) and of Kuhn and Erlos (*Chem. Abs.*, **29**, 6817).

**IV**—Dispersion of photodichroism of various kinds of dyes in gelatin films has been plotted. The various types of dispersion curves obtained can be explained by assuming the presence of two or more absorption bands in the visible region, complexity arising from whether these bands overlap or not and whether they originate from oscillations in the same direction or from those nearly perpendicular to one another as in *x* or *y* bands. C. O. C.

**Relaxation Phenomena in Photodichroism of Organic Dye Gelatin Film.** D. Yamamoto and R. Iwaki. *Kagaku* (*Science*), **21**, 296 (1951); *Chem. Abs.*, **46**, 3886 (10 May 1952).

The long-period relaxation phenomena of dichroism after removing a beam of linearly polarised light on an organic dye–gelatin film were discovered and investigated by Weigert (*Chem. Abs.*, **19**, 1839, 3943). Very short-period (ca. 10 sec.) relaxation phenomena have been found in dye (fluorescein, phloxine, Rhodamine B, Malachite Green, phenosafranine, and Chrysoidin) and gelatin immediately the light is cut off, and they are followed by the long-period ones. These seem to be of a different nature, and may be attributed to the transition from the triplet $T_0^3$ to the singlet $T_0^1$ electronic states of dyes. C. O. C.

**Electric Dichroism of Dye Gelatin Films. III—Theoretical Consideration.** R. Iwaki and D. Yamamoto. *J. Chem. Soc. Japan, Pure Chem. Sectn.*, **72**, 956–958 (1951); *Chem. Abs.*, **46**, 3860 (10 May 1952).

A theory is advanced, which, however, is not in quantitative agreement with experimental results. C. O. C.

PATENTS

**Acylated Aminoacedianthrones—Brown Vat Dyes for Printing.** ICI. *BP* 671,382

The acylated amino derivatives of acedianthrones, e.g. the condensate of aminoacedianthrone with azobenzene-4:4′-dicarboxylic chloride, have excellent printing properties, yielding fast browns when applied with a mild alkali and a reducing agent. C. O. C.

**Daylight-fluorescent Pigments and Coating Compositions.** J. L. Switzer and R. C. Switzer. *BP* 672,763

Daylight-fluorescent coating compositions contain a dye which in weak solution in a transparent solvent, e.g. a finely divided synthetic resin, exhibits both reflected colour and fluorescent colour. The concentration of the dye in the composition must be low enough to prevent dissipation of incident fluorescent energy as heat by the dye molecules, and the depth of the coating (with respect to the direction of incident daylight) must be sufficient to permit the dye to reflect an appreciable amount thereof. There should be not > 0·0005 g. of dye per sq. cm. of coating for any coating composed of a single dye and a carrier. 0·00003–0·00006 g. of dye per sq. cm. of surface covered (at concentrations of < 0·01 g. per c.c. of carrier) gives optimum daylight fluorescence. 0·000015 g. of dye per sq. cm. of surface covered is the minimum amount of dye which shows daylight fluorescence of high chroma or purity of colour, although for tinting there is no practical minimum, as daylight tinting effects have been obtained with only 1 part of dye in many million parts of carrier. C. O. C.

**Pigment Printing of Textiles.** ICI. *USP* 2,579,793–4

Unusually full and even tinctorial value is obtained by using pigment in homogeneous colloidal solution dispersed in an aqueous solution containing two hydrophilic colloids, one of which has been gelled under conditions which leave the other colloid in solution. To render the print wash-fast a water-soluble thermosetting resin is added to the printing paste. C. O. C.

**Fused Outlines on Fabrics for Pattern Cutting.** W. W. Winsen. *BP* 673,407

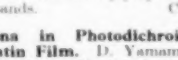
Fabric is printed with a cutting-out pattern in such a way that the material is fused together on the outline, thus eliminating subsequent fraying and the necessity for overstitching. J. W. B.

**Colour Marking of Thermoplastics.** Communications Patents. *BP* 673,366

If the thermoplastic is softened by dielectric heating a suitable colour can be applied by means of a cold die, which may also be an embossing die. Better transfer of the colour is obtained than if a heated die is used. C. O. C.

**Yellow Styryl Dyes as Colour Couplers in Automatic Masking Processes.** ICI. *BP* 673,091

Water-soluble yellow dyes containing a sulphonic or carboxylic acid group, a substituent imparting fastness to diffusion in gelatin, and the grouping

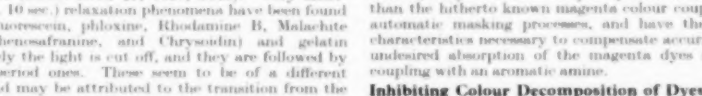


(the terminal C atom is the *ω*-C atom of a cyanoacetyl radical or forms part of a heterocyclic nucleus; the benzene nucleus may be substituted; $R^1$ = Alk subst. with CN, COOAlk, $NO_2$, Hal, OH, O-Alk, COOH, or $SO_3H$; $R^2$ = such a subst. Alk or a subst. or unsubst. hydrocarbon radical) couple much more quickly with aromatic amines than the hitherto known magenta colour couplers used in automatic masking processes, and have the absorption characteristics necessary to compensate accurately for the undesired absorption of the magenta dyes obtained by coupling with an aromatic amine. C. O. C.

**Inhibiting Colour Decomposition of Dyes present in Colour Photographs.** General Aniline. *USP* 2,579,435

A final rinse in an aqueous solution of an addition product of formaldehyde and a urea prevents deterioration of colour photographs, even when kept under hot humid conditions. *USP* 2,579,436

Compounds of formulæ—



($R^1$ = H or $CH_2OH$; $R^2$ = H or Alk; $R^3$ = Alk or alkoxy; Z = bivalent methylene radicals to complete a 5- or 6-membered *cyclo*aliphatic ring) or their formaldehyde addition products are used. C. O. C.

**Colour-corrected Negative Positive Colour Photography.** Kodak. *BP* 672,492

**Forming Separate Colour-component Images by Stripping Photographic Multilayer Film.** Kodak. *BP* 672,582

Imbubition Printing using Yellow Disazo Dyes (IV p. 319).
Coloured Glass Fibres (VIII p. 325).
Fluorescent Materials (VIII p. 326).

## X—SIZING AND FINISHING

**Relative Magnitudes of Surface and Internal Resistance in Drying.** R. E. Peck, R. T. Griffith, and K. N. Rao. *Ind. Eng. Chem.*, **44**, 664–669 (March 1952).

The effects of air velocity and the thickness of the specimen on the time of drying are considered theoretically, taking into account the resistance offered by the air film at the surface of the specimen, and also considering the changes in temp. and diffusivity of the specimen during drying and the effective areas available for diffusion and heat transfer. The derived equations enable the prediction of the effect of air velocity by drying a number of thicknesses, or the effect of thickness by drying at a few velocities, and have been confirmed by experimental observation of the drying of balsa wood slabs. W. K. R.

**Processes for reducing the Shrinkage and Felting Power of Wool.** H. G. Fröhlich. *Textil-Praxis*, **7**, 292–294 (April 1952).

Review with 50 references. C. J. W. H.

PATENTS

**Reducing the Crystallinity of Native Fibrous Cellulosic Material.** U.S. Secretary of Agriculture. *USP* 2,580,491

Cotton or the like is treated in an anhydrous, liquid primary alkylamine of 1–2 C, preferably ethylamine, which

may be mixed with a similar amine of 6–7 C, preferably hexylamine. As much as possible of the liquid is then mechanically removed from the fibre, the remainder being removed by extraction with a non polar solvent. According to the time of immersion the treated material has a crystallinity of 20–50%, the lowest crystallinity being obtained after 4–16 hr. There is no damage to the fibre, which is rendered resistant to combined strain and shock, e.g. in tyre cords, and much less brittle. C. O. C.

**Rendering Cellulose, its Derivatives, Starches, and Related Compounds resistant to Degradation by Acids.** R. R. Dorsett. *USP* 2,580,286

Treatment with a 0·5–3·0% aqueous solution of an alkali-metal molecularly dehydrated phosphate is used; thus cotton cloth padded with 0·5% aq. HCl containing 1% sodium phosphate glass having the composition $Na_2O : P_2O_5$ approx. 1·1 : 1 showed very little degradation when the liquor taken up was dried into it. C. O. C.

**Cord Material for Reinforced Rubber Products.** Industrial Rayon Corpn. *BP* 673,814

Cord material for tyres or other reinforced rubber products, having a denier not > 500, is produced by treating filamentary material with a composition comprising a partial ester of a fatty acid containing not < 12 C with a hexahydric alcohol or its anhydro derivative, e.g. sorbitan monopalmitate, and giving the treated filaments at least 1·5 t.p.m. J. W. B.

**Rendering Fabric Shrink-resistant.** E. Z. Mills. *USP* 2,581,018

Fabric, particularly knitted cotton fabric, is given < 1% residual shrinkage on laundering by passing it in open width and in relaxed condition on a conveyor through a liquid wetting agent. A spreader placed below the surface of the liquor spreads the fabric out without imparting any tension, e.g. the fabric passes below a plate, and air bubbles are directed against the bottom of the fabric to press it against the plate. Finally the relaxed fabric is wound on a hollow roll without imparting tension. The roll is then transferred to a dielectric heater, the roll being used both as an electrode and as a duct for blowing hot air through the fabric. Alternatively the relaxed fabric may be passed continuously through a high frequency electric field. C. O. C.

**Imparting Flame Resistance to Cellulosic Textiles.** American Cyanamid Co. *BP* 671,699

Durable flame resistance with little loss in strength or harshening of handle is produced by impregnation with the following four components—(1) an oxide of Sn and/or Ti and/or Sb and/or Bi, (2) a thermoplastic substance containing not < 20% by weight of combined halogen and rupturing at the C–Hal bonds when heated, (3) a water-soluble salt of an O-containing acid of quinquevalent P, and (4) urea and/or biuret and/or ammonium cyanate and/or ammonium dicyanimide—followed by heating at 135–200° C. One part by weight of the first two components (metallic oxide (1) and halogen compound (0·6–2·0)) is used with 0·2–8·0 parts of the other components (phosphate (1 calc. as $H_3PO_4$) and urea, etc. (1–20)). The components may be applied in the same liquor or two impregnations may be given, one with the first two components and the second with the other components, but in either case the liquor containing the phosphate must have pH 3–10. C. O. C.

**Lustrous, Water-, Crease-, and Spot-resistant Finish for Cellulose Fabrics.** Joseph Bancroft & Sons Co. *BP* 672,673

Cellulose fabrics are rendered water-, crease-, spot-, soil-, and shrink resistant and at the same time lustrous and softer handling by impregnating them with 70–90% on their dry weight of a 5–20% solution of water-soluble thermosetting resin-forming materials and an acid catalyst, drying, cooling, calendering at 100–200° F., and then baking at 250–350° F. for 8–2 min. C. O. C.

**Linen-like Finish on Cotton and or Spun Rayon Fabrics.** Joseph Bancroft & Sons Co. *BP* 672,674

A linen-like finish is imparted to fabrics containing 100–50% spun regenerated cellulose fibres and 0–50% cotton by impregnating them with 70–90% on their dry weight of a 5–20% aqueous solution of water-soluble thermosetting resin-forming material and an acid catalyst, drying to 10–15% free moisture content, cooling to room temperature, passing through a chasing calender whose rolls are at 250–300° F. so as to heat the fabrics to 100–200° F., there being several thicknesses of the fabric in each nip of the calender, and finally baking at 250–350° F. for 8–2 min. C. O. C.

**Imparting Very High Lustre while preserving Weave Characteristics.** Bleachers' Assocn. and Lockers (Engineers). *BP* 673,014

The fabric while being treated in a beater of the type described in *BP* 669,987 (*J.S.D.C.*, **68**, 283 (July 1952)) is led back and forth between the rollers of a bank of two or more rollers arranged vertically above one another beneath the beater, so that the beating action is transmitted through the fabric from one roller to another and acts upon the fabric each time it passes between adjacent rollers. Thus a single vibrator applies a succession of compressions or impacts to a continuous length of fabric. C. O. C.

**Alkali-soluble Cellulose Sulphate.** Courtaulds. *BP* 670,346

Cellulose treated with cyanamide and sulphuric acid to form the sulphate is impregnated with an aqueous alcoholic solution of a water-soluble salt of a multivalent metal and dried. The resulting material is insoluble in water but soluble in weakly alkaline solutions. Yarn so treated is useful as a carrier or core yarn in making effect threads or fabrics. W. G. C.

**Rubberised Plies for Tyres.** Dan River Mills. *BP* 671,394

Individual cords are pretensioned to remove stretch variations, impregnated or coated with a rubber-compatible bonding material, stressed by longitudinal tension and/or lateral compression further to remove residual stretch variation, and dried while in this state to set the bonding material. Rubber is then calendered directly on to both sides of a sheet made from a number of such cords. J. W. B.

**Setting Keratinous Fibres without Damage.** Procter & Gamble Co. *BP* 672,837

A composition for setting animal fibres, e.g. in hair waving, includes a softener for reducing harshness and strength loss, and comprises essentially a water-sol. thiol and a water-sol. salt of a thiosulphuric acid of formula $R{\cdot}S{\cdot}SO_3H$ (R = organic radical), the molar ratio mercaptan : thiosulphate being > 1 : 1. Alternatively it may comprise the mixture of products, in similar ratio, from the reaction between a water-sol. organic disulphide $R^1{\cdot}S{\cdot}S{\cdot}R^2$ ($R^1$ and $R^2$ = organic radicals with C linked to S) and a water-sol. hydrosulphite. The pH is kept at 7·10·5. Thus dithioglethanol (5·0 parts by wt.), $Na_2S_2O_4$ (6·0), ammonium hydroxide containing 28% $NH_3$ (8·6), and water (80·4) are allowed to stand until the pH is 9·5. When used to wave human hair a tight curl can be obtained with no perceptible damage.

*BP* 672,838

A composition for setting hair without damage comprises a water-sol. thiol and a water-sol. salt of a thiosulphuric acid $R{\cdot}S{\cdot}SO_3H$ (R = organic radical), the molar ratio thiosulphate : mercaptan being > 1 : 1. J. W. B.

**Softening Sulphur-containing Scleroproteins.** Henkel & Cie. *BP* 672,730

Sulphur-containing scleroproteins, e.g. keratin, may be reshaped by softening with a solution of a dialkyl thiocarbonate and then removing the softener by reoxidation or treatment with aldehydes or alkylene dihalides. Thus biscarboxymethyl trithiocarbonate (10 g.) is dissolved in water, strong ammonia added (15 ml.), and the vol. made up to 100 ml. Human hair, suitably rolled, is moistened with this soln., and maintained at body heat for 1 hr., after which the reagent is removed by repeated peroxide washings. J. W. B.

**Polybutadiene for Reducing the Felting Properties of Wool.** Montclair Research Corpn. and Ellis-Foster Co. *USP* 2,580,602

Wool impregnated with a non-vulcanised, non-tacky aqueous emulsion of a synthetic butadiene polymer (obtained by oxidising an ordinary aqueous emulsion of butadiene polymer) has its felting properties greatly reduced without impairment of its handle, draping properties, or resistance to creasing. C. O. C.

**Rendering Wool Alkali-resistant with Divinyl Sulphons.** United States Rubber Co. *USP* 2,579,871

Proteins treated with vinyl sulphone at room temperature are given good stability to heat, water, solvents, and alkali. Thus wool treated with vinyl sulphone can be dyed in alkaline vats. C. O. C.

**Rendering Acetate Rayon and other Textiles more resistant to Heat.** Société Rhodiacéta. *BP* 672,716

The safe ironing temperature of acetate rayon is raised to 250°C. by treatment with a compound of formula $SiX^1X^2X^3X^4$ ($X^1$, $X^2$, $X^3$, $X^4$ = same or different Hal or acyloxy) dissolved in an organic solvent which has no solvent action on, but is preferably a swelling agent for, the acetate rayon, the strength of the solution being not > 10%. It is unnecessary to add a substance which combines with the acid liberated. C. O. C.

**Coated Sheet Materials with Embossed Designs.** American Viscose Corpn. *BP* 673,129

Coated fibrous sheet material is obtained by making a film of thermoplastic material adhere to a surface of fibrous web consisting of carded or haphazard fibres containing 10–40% of thermoplastic fibres. The film and fibrous web are pressed together so as to compress the web only slightly; selected areas are pressed further, using enough heat to make the film and the thermoplastic fibres adhesive. On cooling, a permanent embossed design is obtained. J. W. B.

**Impregnated Materials incorporating Parallel Fibres.** Minister of Supply. *BP* 673,367

Sheet or strip material containing parallel overlapping fibres or rod-like material, e.g. asbestos-reinforced resin, is made by impregnating a mass of fibres or similar elements with a liquid which acts as a lubricant and which may also be water-sol. and/or heat-hardenable, and extruding through a slit in a direction normal to that of the applied pressure. J. W. B.

**Curing Coatings of Polysulphide Polymers.** Thiokol Corpn. *USP* 2,584,264

Coatings containing a polyalkylene polysulphide containing > 1 SH group attached to carbon which is liquid at 25°C. and Zn chromate or peroxide are cured by treatment with gaseous ammonia or a volatile amine. The resultant coatings are immune to the action of organic solvents. C. O. C.

Improving the Dyeing Properties of Fur boiled in Sulphuric Acid (VI p. 324).
Polyester-Hydrolysed Leather Compositions (XII p. 331).

## XI—PAPER AND OTHER CELLULOSIC PRODUCTS

**Yellowing of Paper.** E. Liebert. *Allgem. Papier-Rund.*, 93–94, 96–97 (1952); *Chem. Abs.*, **46**, 4231 (10 May 1952).

With nearly all rag halfstuffs, brightness improved with irradiation. Yellowing of wood pulps decreased with decreasing lignin content. Well bleached wood pulps did not yellow on extended irradiation, whereas unbleached wood pulps showed marked yellowing. Bleached mechanical pulp rapidly loses brightness even with short irradiation. Fillers may influence the rate of yellowing. C. O. C.

**Aniline Dyes in the Paper Industry.** B. Cornely. *Allgem. Papier-Rund.*, 856–858 (1951); *Chem. Abs.*, **46**, 4227 (10 May 1952).

Historical. C. O. C.

**Kinetics of the Decomposition of Solid Cotton Cellulose in a High-frequency Electromagnetic Field.** B. A. Zakharov. *Doklady Akad. Nauk S.S.S.R.*, **81**, 417–419 (21 Nov. 1951): long abstract (German) with diagrams in *Faserforsch. und Textiltech.*, **3**, 154–155 (April 1952).

High-frequency (10 megacycles) dielectric heating is applied to cotton cellulose contained in a quartz tube, the temp. of the cotton being determined by means of a thermocouple. The decomp. is followed by measuring the loss in wt. of the cotton; the volatile decomp. products are passed into a cooled receiver (73% of these condense) and are examined. Curves are given showing the progress of the decomp. with time and rise in temp. Severe decomp. sets in when the temp. rises above 200°C. (4 min.) and amounts to 80–85% over the range 300–600°C. The condensate contains 28% of reducing substances, and after hydrolysis a further 28% of carbohydrate matter is obtained. When decomp. is carried out under the usual conditions of convection heating, carbohydrate matter is obtained only when reduced pressures are used. A. E. S.

**Chemical Changes produced in the Cellulose Macromolecule by Oxidising Agents. IV—Lactone Linkages in the Oxycellulose Macromolecule and their Effect on the Estimation of Carbonyl Groups by the Hydroxylamine Condensation Method.** E. D. Kaverzneva and A. S. Salova. *Izvestiya Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 782–790 (Nov.–Dec. 1951); **V—Proof of the Existence of α-Hydroxymonoketone Groups in Oxycelluloses.** E. D. Kaverzneva. *Ibid.*, 791–794 (Nov.–Dec. 1951); **VI—Presence in Oxycelluloses of Carbonic Ester Groupings and their Effect on the Estimation of Uronic Carboxyl Groups.** E. D. Kaverzneva, V. I. Ivanov, and A. S. Salova. *Ibid.*, 185–189 (Jan.–Feb. 1952).

Further experimental evidence is brought forward in support and amplification of the general conclusions already reached (*J.S.D.C.*, **67**, 397 (Oct. 1951)) concerning the groupings present in oxycelluloses. The presence of the postulated ester (lactone) groupings is detected in several preparations by the formation of a pink coloration on treating with hydroxylamine in alkaline soln. (formation of hydroxamic acid), and then with $FeCl_3$. A positive reaction is given by cellulose oxidised with hypochlorite (pH 4-6, 7, 11, or 9-5), with hydrogen peroxide (pH 4-6), with air in cuprammonium soln., or with nitrogen dioxide. A negative or insignificant reaction is given by cellulose oxidised with hydrogen peroxide in neutral or alkaline soln., or with periodic acid. It is shown that the lactone linkages present in cellulose oxidised in alkaline soln. are formed not during the actual oxidation reaction, but during the subsequent acid demineralisation treatment. The conditions necessary for the formation of hydroxamic acids by the action of hydroxylamine on oxycelluloses are examined, cellulose, cellulose acetate, and coumarin being used for comparison purposes. Under the conditions necessary for oxime formation (pH 5–6), some hydroxamic acid is formed, and consequently, the hydroxylamine method for determining the carbonyl content of oxycellulose gives results that are too high. The experiments previously described (*loc. cit.*) on the reduction of the product of the reaction of an oxycellulose (after elimination of CHO groups) with hydroxylamine are extended. In the final hydrolysate, in addition to primary amines, which have their origin in ketone groups, ammonia was detected; this is considered to arise from the decomp. of amides formed by the reduction of hydroxamic acids, and its formation provides further evidence of the presence of lactone groupings. Detailed experimental evidence is given for the presence of $CH(OH)\text{-}CO$ groupings (see *loc. cit.*) in oxycelluloses other than those obtained by the use of periodic acid. The specificity of the phosphomolybdate reaction used is demonstrated by tests on various organic compounds. Further examination of the high "uronic" carboxyl content compared with the "total" carboxyl content (see *loc. cit.*) for cellulose oxidised with hypochlorite in acid or neutral soln. indicates that in addition to carboxyls masked by lactone formation there are also a small number of carbonic ester groupings present, which account for a part of the discrepancy. These are considered to be formed from oxidised glucose residues containing a CO in the 2-position; further oxidation leads to the breaking of the 1–2 bond and the formation of a carbonic ester grouping linking the residues. This grouping is very unstable, being hydrolysed by dil. alkali in the cold and by dil. acid on warming; it is in fact detected by treating the oxycellulose with carbonate-free NaOH soln., acidifying, and blowing out any $CO_2$ formed, the whole process being carried out in the cold. The presence of carbonic ester groupings partly explains the instability to alkalis of oxycelluloses prepared in acid soln. A. E. S.

**Effect of Metal Ions on the Visco-elastic Characteristics of Ethyl Cellulose.** S. A. Glikman and O. G. Efremova. *Doklady Akad. Nauk S.S.S.R.*, **81**, 1089–1092 (21 Dec. 1951).

Preparations of ethyl cellulose containing varying

amounts of Ca (< 0·001–0·23%) and Fe (0·007–0·139%) are obtained by repeated precipitation of the commercial material from an acetone soln. of HCl (low Ca and Fe content) and by precipitating this or the commercial material from a soln. to which small amounts of aq. $Ca(OH)_2$, aq. $FeCl_3$, or colloidal $Fe(OH)_3$ have been added. Some observations are made on the rheological behaviour of solutions of these preparations, and the properties of a 10% gel in dibutyl phthalate are studied in detail. The effect of the presence of Fe and Ca in concentrations comparable with those commonly found in practice is to increase considerably the elastic moduli, the elastic limit, and the viscosity figures for the gel. It is considered that multivalent metal ions are taken up by carboxyl groups present in ethyl cellulose and that intermolecular linkage is thereby strengthened. A. E. S.

**Allyl Hydroxyethyl Celluloses and their Copolymerisation with Sulphur Dioxide. I and II.** S. N. Ushakov and O. M. Klimova. *J. Appl. Chem. U.S.S.R.*, **25**, 46–56 (Jan.); 191–196 (Feb. 1952).

Previous work by Ushakov and Orlova has shown that allyl esters of cellulose, prepared by the heterogeneous allylation of alkali cellulose with allyl bromide, react with $SO_2$ to give three-dimensional condensates containing combined $SO_2$ equiv. to the allyl content of the preparation. Heteropolymerisation will occur also with monomers that are themselves capable of polymerisation, but, as this latter reaction and the heteropolymerisation will occur simultaneously, such processes are unsuitable for theoretical study. The use of $SO_2$ leads to a product that is markedly different in properties from the starting material and is readily separated in a pure form. The aim of the present work is to study the relation between the degree of cross linking in the copolymer and its properties. For this purpose, the product of heterogeneous allylation is unsuitable, but it is found that the introduction of a small proportion of hydroxyethyl groups confers solubility in alkali and enables allylation to be effected in a homogeneous manner. The first paper is devoted to the preparation and properties of ethers of this type. Those prepared contain 0·05–0·3 hydroxyethyl and 0·07–1·5 allyls per glucose residue. They react with atmospheric oxygen, probably with the formation of an –O·OH group on the carbon adjacent to the allyl double bond. It is considered that the resulting side-chain oxidises another allyl side-chain to an epoxide and is itself converted into a semiacetal, which is hydrolysed with liberation of acrolein. Acrolein is in fact obtained in 71% yield. Allyl hydroxyethyl celluloses undergo cross-linking reactions in presence of benzoyl peroxide, but, owing to spatial factors, the process is very incomplete. The second paper deals with the reactions of seven allyl hydroxyethyl cellulose preparations with $SO_2$ in presence of silver nitrate as catalyst. The numbers, *b* and *a*, of hydroxyethyl and allyl groups respectively per glucose residue in the preparations are—*b* 0·05, *a* 0·07 and 1·49; *b* ~ 0·14, *a* 0·26 and 1·41; *b* 0·95, *a* 0·11, 0·50, and 0·72. The freshly precipitated ether (1 part by wt.) is placed in a tube, silver nitrate (0·01) added in alcoholic soln., the mixture cooled to 10–12° C., and liquid $SO_2$ (20–22) added. The tube is sealed, and maintained at 18° C. for 18 hr., and then at 40° C. for 6 hr. The copolymer formed dissolves in the excess $SO_2$, and the final result is a continuous turbid gel. The product is washed and dried. It is analysed for combined S, and its behaviour towards various solvents is examined. Of the solvents that dissolve or swell the original ether, only pyridine has any notable effect on the copolymer. The amount of combined S is always close to that required for polysulphone formation with full participation of the allyl groups. At $a > 0{\cdot}5$, the product is insoluble in all the usual solvents; at $a \sim 0{\cdot}26$, the product swells somewhat in pyridine; at $a \sim 0{\cdot}07$, it swells strongly and partly dissolves in pyridine, though the dissolved part is found to be substantially free from allyl and S, indicating the inhomogeneity of esters with a low degree of substitution. The copolymers dissolve in conc. $H_2SO_4$ and $HNO_3$, with the formation of an appreciable charred residue. A. E. S.

**Heterogeneous Hydrolysis of Cellulose Triacetate.** F. S. Sherman and I. O. Goldman. *J. Appl. Chem. U.S.S.R.*, **25**, 84–89 (Jan. 1952).

Fibrous cellulose triacetate, made by heterogeneous acetylation, yields stronger and more stable films than the usual secondary acetate, made by homogeneous acetylation followed by hydrolysis. However, the low elasticity of the films limits their use. After slight hydrolysis (reduction of the combined acetic acid from 62% to ~ 60%), fibrous triacetate yields films of satisfactory elasticity. Heterogeneous hydrolysis with dil. $HNO_3$ in the cold (e.g. N. acid for 24 hr.) gives good results, and it is shown that the treatment does not affect the degree of polymerisation of the material (mol. wt. ~ 132,000). None of the hydrolysed products obtained (51–60% combined acetic acid) is completely sol. in acetone. A. E. S.

PATENTS

**Pigmented Cellulosic Pulp.** R. T. Vanderbilt Co. *USP* 2,583,548

A highly pigmented product is obtained by adding dry paper pulp to dil. aq. $CaCl_2$, $BaCl_2$, or $ZnCl_2$, beating the resulting mass for a prolonged time, and then precipitating the Ca, Ba, or Zn as an insoluble pigment. C. O. C.

**Machine-glazed Paper.** British Bewond Co. *BP* 672,142

In making machine-glazed paper a size is used comprising an aqueous colloidal dispersion of a rosin with or without addition of finely divided inert material, e.g. kaolin, in which the rosin is treated with lime or has not > 5% by wt. of calcium resinate added to bring its m.p. above 100° C. This enables a higher temperature, e.g. well above 100° C., to be used for the drying cylinder, with improvement in the resulting product, allowing increased peripheral speed of the cylinder, thus raising the output of the machine. S. V. S.

**Plasticised Supercalendered Glassine Paper.** Riegel Paper Corpn. *BP* 673,526

Plasticised, supercalendered glassine paper is produced by applying to glassine paper a plasticising composition containing invert sugar as its principal plasticiser, supercalendering the paper at high temperature, cooling rapidly to < 140° F. by directing cold air against both sides of the paper as it leaves the supercalender rolls, and winding into a roll. Use of invert sugar prevents excessive water absorption and retention whilst conferring desirable hygroscopicity and plasticity on the paper. For paper for use under conditions of high humidity the plasticising composition consists essentially of invert sugar, but for conditions of low humidity a small proportion of a liquid plasticiser is added. S. V. S.

**Siloxane-impregnated Tissue Paper.** Dow Corning. *BP* 673,422

Tissue paper is impregnated with 5–12% of a liquid siloxane, which contains an average of 1·75–2·25 univalent alkyl and/or aryl hydrocarbon radicals per silicon atom. The paper, which does not fuel or look greasy, may be used as lens- or glass-cleaning and -polishing tissue, or as non-wetting cigarette paper. S. V. S.

**Coated Paper.** United States Rubber Co. *BP* 673,872

To impart a gloss coating to paper, an aqueous dispersion of an amorphous thermoplastic polymeric material is applied, having a second-order transition temperature at 40–125° C., and comprising a resinous copolymer of styrene and acrylonitrile in proportions from 65 : 35 to 80 : 20, removing the water from the coating, and hot-calendering at a temperature above the second-order transition temperature. The polymeric material forming the coating may consist of a mixture of the above-mentioned resinous copolymer and a rubberlike copolymer (Buna N) of 1:3 butadiene and acrylonitrile in proportions from 50 : 50 to 95 : 5. The penetration of the solids of the aqueous dispersion into the paper does not exceed 20% by wt. of the polymeric material content of the dispersion, and the coating exhibits a resistance to water vapour transmission of not > 5 g. of water per 100 sq. cm. per 24 hr. when exposed at 90° F. and at least 95% R.H. S. V. S.

**Paper resistant to Ink Bleed.** National Cash Register Co. *USP* 2,581,186

Natural or synthetic zeolites capable of absorbing oil are useful for coating paper to impart resistance to ink bleed, much less of them being needed than of the agents previously used. C. O. C.

**Modified Urea Formaldehyde Resin for Paper Sizing.** American Cyanamid Co. *USP* 2,582,840

Incompletely polymerised, negatively charged, partly or completely neutralised sulphonated bishydroxymethylurea

resins in aqueous solution can be flocculated or precipitated by adding acid to bring them to pH < 6·5. This process is used in sizing paper stock. C. O. C.

**Mineral-coated Paper.** Monsanto. *USP* 2,583,274

Styrene–alkyl acrylate copolymers are very efficient bonding agents for pigment or mineral coatings for paper. The coated paper has high brightness, high gloss, and good affinity for printing inks. C. O. C.

**Drying Films of Regenerated Cellulose or other Hydrophilic Material.** La Cellophane. *BP* 673,255

Several films in superposition are dried at the same time after they have been treated before entering the drier with a substance, e.g. 10% aq. glycerol containing 0·5 g. Na silicate per litre, which reduces the tendency of the dried films to stick together. C. O. C.

**Sheets of Regenerated Cellulose.** La Cellophane. *BP* 673,234

Addition to either the viscose or the coagulating bath of a cationic surface-active compound avoids clogging of the extrusion aperture, results in fewer breakages in the gel as it leaves the extrusion aperture or in the treatment baths, and yields an improved product. C. O. C.

**Organosilicon Derivatives of Cellulose.** Dow Corning. *BP* 671,721

Tri-organosilyl derivatives of cellulose having an average of 0·25–2·0 tertiary silyl groups per glucose unit of the cellulose (prepared by treating an incompletely esterified or etherified cellulose having 1·0–2·75 ester or ether groups per glucose unit with a compound of formula $R_3SiAr_2Hal$ (R = Alk or Ar)) are suitable for moulding, extruding, or casting. C. O. C.

Sodium Salts of Pectin and of Carboxymethyl Cellulose in Aqueous Sodium Chloride. I—Viscosities. II—Osmotic Pressures (III p. 313).

Anticorrosion Properties of Aluminohexacellulose (V p. 322).

## XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

**Hydration of Collagen and Leather.** C. H. Spiers. *J. Soc. Leather Trades Chem.*, **36**, 20–25 (Jan. 1952).

The real volumes of collagen, chrome-tanned leather, and vegetable-tanned leather are measured by means of the author's direct-reading volumenometer (*J. Sci. Instrum.*, **11**, 216 (1934)) at various moisture contents, and the real densities obtained. Dry collagen has a density of 1·22 g./ml., agreeing with a theoretical value of 1·23 given by Astbury and Atkin (*Nature*, **132**, 348 (1933)), and vegetable- and chrome-tanned leathers 1·38 and 1·33 respectively. As the materials hydrate the real densities increase to constant values of 1·40 for collagen, 1·43 for vegetable-tanned leather, and 1·48 for chrome leather. The volume increase on hydration is less than the vol. of water taken up, the compression being very great initially (e.g. tenfold for collagen, ca. fivefold for leather), falling to a constant value of 1·7 for all three at higher moisture contents. It is considered that water is absorbed on side-chain amino groups, and that collagen is made less hydrophilic on tanning. Vegetable tannin, which combines with side-chain amino groups, has a more marked effect than chrome, which combines with side-chain carboxy groups. A. J.

**Shrinking of Dry Collagen.** G. I. Kutyanin. *Doklady Akad. Nauk S.S.S.R.*, **82**, 405–408 (21 Jan. 1952).

Collagen—(*a*) untanned, (*b*) tanned with a vegetable extract, and (*c*) tanned with chrome—is allowed to shrink in the wet and in the dry condition under the action of heat. The wet collagens give shrinkage temperatures of (*a*) 70, (*b*) 80, and (*c*) 120°c. The dry collagens also show shrinkage effects. Their length–temp. curves are very similar, showing a rapid fall at ~ 110°c., followed by a gradual fall to ~ 210°c., when a final rapid fall sets in. However, the temperatures for complete shrinkage vary—(*a*) 220, (*b*) 250, and (*c*) 260°c. The observations are interpreted in terms of the effect of heat and water on the intermolecular forces and linkages present in tanned and untanned collagen. A. E. S.

**Enzyme Unhairing.** O. Grimm. *Leder*, **2**, 265 (1951); *J. Amer. Leather Chem. Assocn.*, **47**, 300 (April 1952).

Enzyme unhairing is reviewed. This unhairing, according to our present knowledge, depends on the action of proteolytic enzymes on the lower layers of the epidermis. The true hide fibre substance is not attacked. Leather quality may require an alkaline swelling, either before or after loosening of the hair. C. J. W. H.

**Dyeing of Leather.** A. Simoncini. *Boll. Staz. sper. Industr. Pelli, Mater. conciants.*, **27**, 42 (1951); *J. Amer. Leather Chem. Assocn.*, **47**, 375 (May 1952).

A discussion of the types of dyes used for leather, with details of the differences in their chemical nature and method of application. C. J. W. H.

**Aniline Finishes, Lacquers, and Lacquer Emulsions.** W. Pohl. *Shoe and Leather Reporter*, **204**, (3), 23 (1952); *J. Amer. Leather Chem. Assocn.*, **47**, 298–299 (April 1952).

Lacquer finish, saturated with aniline dyes or with lakes, gives the leather a fuller body and more lively appearance yet retains the aniline effect and satisfactory covering qualities. Lacquer emulsions reduce the risks of resulting brittleness but have the disadvantage of lower fastness to wet rubbing. This can be overcome by suitable top dressings. Aniline finishes have an advantage over pigment finishes in that they permit retention of the natural grain effect. C. J. W. H.

**Chemistry of the Carrotting of Rabbit Fur.** P. Huckel and H. G. Frohlich. *Textil Praxis*, **7**, 381–385 (May 1952).

Mercuric and non-mercuric carrotts are compared, and tests are described on various qualities of rabbit fur which have been examined for swelling properties, acid-binding power, alkali solubility, cystein content, and behaviour towards Folin's reagent (prepared from molybdenum-free sodium tungstate and phosphoric acid). With mercuric carrotts care has to be taken that the skins are carefully piled on top of each other after treatment, as exposure to light during drying can give rise to red patches. With non-mercuric carrotts, the drying temp. should not exceed 70°c., as otherwise residual hydrogen peroxide may cause fibre damage. The cystein content of the tips of both mercuric and Aurofelt (nitric acid, metallic catalyst, and hydrogen peroxide) carrotts is brought below 5%. The alkali solubility and swelling of the fibre tips of Aurofelt carrotts are greater than with mercuric carrotts, and the latter result in the incorporation of Hg in the protein structure of the fur. The existing differences between the tips and remainder of the fur fibre are accentuated by carrotting. B. K.

**Action of Nickelammonium Hydroxide on Proteins.** J. W. Bell and C. S. Whewell. *J.S.D.C.*, **68**, 305 (Aug. 1952).

PATENT

**Polyester Hydrolysed Leather Compositions.** ICI. *BP* 671,398

Mixing an organic poly*iso*cyanate-modified polyester with partly hydrolysed leather gives a tough, flexible, flexing-resistant, and abrasion-, oil-, and solvent-resistant material. Thus, vegetable-tanned leather dust (175) is boiled with water for 30 min., and filtered to give a pulp containing 50% $H_2O$. This is gradually added to an organic poly*iso*cyanate-modified polyester (150) running on a rubber mill at 50°c. After water has dried off, a tough plastic composition is obtained, and is mixed with a mixture (200) of equal vol. of acetone, benzene, toluene, and ethyl alcohol, and the mix is compounded with hexa(methoxymethyl)melamine (15), 2:4-dichloro-1-naphthol (1·5), tritolyl phosphate (15), yellow chrome pigment (15), and Cu phthalocyanine pigment (9). This is spread on a cotton fabric, the solvent then being evaporated, and cured for 2 hr. at 125°c. J. W. B.

Effect of Ammonium and Potassium Salts on the Stability and Viscosity of Solutions of Rennet Casein (VI p. 324).

# XIII—RUBBER; RESINS; PLASTICS

**Macromolecular Compounds. XL—Relative Tendencies of Macromolecules of Various Lengths to undergo Degradation.** V. V. Korshak. *Izvestiya Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 753–755 (Nov.–Dec. 1951). **XLI—Alcoholysis of Polyesters.** V. V. Korshak and S. V. Vinogradova. *Ibid.*, 756–760 (Nov.–Dec. 1951).

**XL**—The author has shown from experiments on polyamides, polyesters, and polyphenylenemethyls that the probability that a given linear macromolecule will undergo fission during attack by degrading agents of various kinds is directly proportional to the length of the molecule. It is now shown how this relationship follows from elementary statistical considerations.

**XLI**—The kinetics of the alcoholysis of polyhexamethylene sebacate by means of cetyl alcohol is studied. It is shown to be in accordance with the theory advanced above, relatively rapid degradation occurring in the early stages with the consumption of only small amounts of cetyl alcohol. A. E. S.

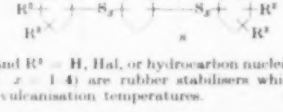
**Macromolecular Compounds. XLII—Transarylation Reaction of Diarylalkanes.** G. S. Kolesnikov and V. V. Korshak. *Izvestiya Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 761–770 (Nov.–Dec. 1951).

Details are given of the experiments upon which the results already reported (*J.S.D.C.*, **67**, 48 (Jan.) and 293 (July 1951)) are based. A. E. S.

PATENTS

**Stabilising Rubber with a Mixture of a Phenol Sulphide and Tervalent Antimony Oxide.** Firestone Tire & Rubber Co. *USP* 2,581,930

A mixture of tervalent antimony oxide and a compound of formula—



(R$^1$, R$^2$, and R$^3$ = H, Hal, or hydrocarbon nuclei of < 9 C; $n$ = 0–3, $x$ = 1–4) are rubber stabilisers which do not react at vulcanisation temperatures. C. O. C.

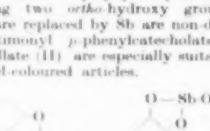
**Tin or Antimony Salts of Phenol Reaction Products as Stabilisers for Rubber.** Firestone Tire & Rubber Co. *USP* 2,581,931

Tin and antimony salts of compounds of formula Ph·CR$^1$R$^2$·Ph (Ph = phenol residue; R$^1$ and R$^2$ = H, Alk, or Ar), e.g.—

are non-discolouring rubber stabilisers. C. O. C.

**Stabilising Acrylonitrile 1:3-Butadiene Copolymers.** Firestone Tire & Rubber Co. *USP* 2,581,909–11

Antimonyl derivatives of polyhydroxy aromatic compounds containing two *ortho*-hydroxy groups whose hydrogen atoms are replaced by Sb are non-discolouring stabilisers. Antimonyl *p*-phenylcatecholate (I) and antimonyl pyrogallate (II) are especially suitable for use in white or pastel-coloured articles.



(I) (II)

C. O. C.

**Stabilised Vinyl Chloride Resin Films.** Firestone Tire & Rubber Co. *USP* 2,581,915

Incorporation of 0·25–5·0% of a cadmium dialkyl mercaptide, each of whose alkyl groups has 5–22 C, into vinyl chloride polymers or copolymers stabilises them to heating and ageing. C. O. C.

**Terephthalamide Derivatives.** American Viscose Corpn. *BP* 671,141

Compounds useful for producing synthetic resins and fibres are obtained by ammonolysis of esters of terephthalic acid; *NN'*-bis-β-hydroxyethylterephthalamide is made by heating diethyl terephthalate with monoethanolamine. W. G. C.

**Polyester Copolymers.** Texas Co. *USP* 2,584,315–6

Chemically inert, thermally stable coating compositions are obtained by the use of copolymers of a diallyl phthalate and/or tetrahydrophthalate and/or chlorotetrahydrophthalate and an unsaturated mixed polyester in which a dihydroxyalkane or alkene of > 1 C is esterified with two dibasic acids. One of the dibasic acids is aromatic, while the other is an α-olefinic unsaturated dibasic acid. C. O. C.

**Carboxyphenylsilanes.** Dow Corning. *BP* 670,923

Compounds of formula (HOOC·C$_6$H$_4$)$_2$Si(CH$_3$)$_2$ are useful in the preparation of copolymers of the polyamide or alkyd type; e.g. bis-*p*-carboxyphenyldimethylsilane is obtained by carbonating the Grignard reagent of bisbromophenyldimethylsilane. W. G. C.

**Plasticisers for Film-forming Substances.** Basf. *BP* 673,405

Compounds of formula R$^1$·O·CO·O·[CH$_2$]$_x$·O·CO·O·R$^2$ (R$^1$ and R$^2$ = Cl-containing aliphatic radicals of 6–18 C in all), e.g. the *bis*(α-dichlorobutyl carbonate) of 1:4-butanediol, are useful plasticisers for natural and synthetic resins, cellulose esters, etc. C. O. C.

Antistatic Treatment of Vinyl Resins (III p. 314).

Dispersions of Polymeric Tetrafluoroethylene (III p. 314).

Hydro-polyalkoxysilyl Addition Products of Rubber (III p. 314).

Fibre- and Film-forming Copolymers of Dichlorodifluoroethylene and Ethylene (VI p. 324).

Organosilicon Derivatives of Cellulose (XI p. 331).

# XIV—ANALYSIS; TESTING; APPARATUS

**Determination of Free Chlorine.** A. E. Whitlock. *Lab. Practice*, **1**, 73–76 (May 1952).

Seven procedures are fully described, using—(i) o-tolidine (colorimetric), (ii) o-tolidine–arsenite (colorimetric), (iii) iodometry (titrimetric), (iv) methyl orange in acid soln. (titrimetric), (v) Chlorotex (B.D.H. reagent), (vi) ammonium ferrous sulphate (titrimetric), and (vii) phenylarsinoxide reagent (electrometric). By using methods (iii) and (iv) in conjunction it is possible to differentiate between free and combined available chlorine when the total concn. is > 1 p.p.m., whilst for lower concn. the joint use of methods (i) and (ii) furnishes similar distinction. The four forms in which free chlorine usually occurs in water supplies may be differentiated and separately estimated by method (vi). In the absence of $NCl_3$, the other three forms may be similarly distinguished by method (vii). J. W. D.

**Determination of Free Chlorine in Water by means of *o*-Dianisidine Dihydrochloride Reagent.** K. L. McEwen and G. A. Grant. *Canadian J. Technol.*, **30**, 66–71 (April 1952).

**Colorimetric Microdiffusion Determination of Chloride—Application to Chlorinated Insecticides.** H. T. Gordon. *Anal. Chem.*, **24**, 857–862 (May 1952).

In an adaptation of the Conway microdiffusion method, chlorine is liberated from chlorides by direct oxidation with $KMnO_4$ (organic chlorine is first converted to chloride by the action of sodium n-propoxide); it diffuses into a soln. of Fast Green, which is quantitatively decolorised, and the change in colour intensity is followed photometrically. For routine work a standard Spekker curve may be prepared. The limit of sensitivity of the method is ~ 0·1 μg. chlorine, though under favourable conditions it may be as low as 0·005 μg. The method, which is given in full detail, is discussed primarily in connection with insecticides, but it is applicable to any substance containing alkali- or oxidant-labile chlorine. Bromine may also be estimated by this method. J. W. D.

**Estimation of Tenths of a Microgram of Copper.** R. H. Lambert. *Anal. Chem.*, **24**, 868–870 (May 1952).

The method is based on the catalytic effect of traces of Cu upon the darkening, through autoxidation, of soln. of resorcinol. The resorcinol is used as a 5% soln. in *n*-isopropanol, and the reaction is carried out at 25° C. for exactly 30 min., a pH of 12 being maintained by means of a phosphate buffer. At the end of the reaction time the oxidation is arrested by lowering the pH with glacial acetic acid. The developed colour intensity is measured photometrically at 395 mμ. Best results are obtained if controls are run simultaneously, under which conditions accurate temp. control is less important.

Over the range 0–1·0 μg. Cu per 25 ml. soln., the accuracy is ± 0·05 μg. In determining 0·5 μg. Cu, 2 μg. Ag or 50 μg. Fe causes interference, both metals having some catalytic effect upon the reaction. Al, Mg, and Sn slightly inhibit the oxidation, but Pb, Hg, Ca, Cd, and Zn do not interfere. Al shows turbidity. The development and details of the procedure are described in full.

J. W. D.

**Extraction and Colorimetric Determination of Iron by means of 8-Hydroxyquinoline.** A. G. Hamlin. *J. Textile Inst.*, **43**, T 234–T 246 (May 1952).

A method is devised and described whereby small amounts of $Fe^{+++}$ are determined by absorptiometric estimation of the ferric oxinate extracted from aq. soln. by chloroform. Careful control avoids interference by almost all other ions likely to occur in textile materials, Zr and V being exceptions if present in moderate amounts. Copper is easily removed from the $CHCl_3$ extract by KCN washing. Some metals, e.g. Al, Cr, Zr, are found to promote sequestration or reduction of Fe when strongly acid soln. of the metals are neutralised in presence of tartrate. Such reduction is the main source of error, but the defect is offset by wide applicability. J. W. B.

**Quantitative Determination of Sodium Cetyl Sulphate in its Solution in Water.** G. R. Edwards, W. E. Ewers, and W. W. Mansfield. *Analyst*, **77**, 205–207 (April 1952).

Existing titrimetric methods for estimating sodium cetyl sulphate in aqueous soln. are effective for concn. > 0·001 M. (340 mg./litre); the procedure described may be used for concn. as low as 10 mg./litre. The compound of detergent with methylene blue (used as its hydrochloride) is ppt., filtered, and washed on a column packed with ground quartz, dissolved in ethanol, and determined photometrically. There is a straight-line relationship between light absorption and concn. over the range 10–40 mg. sodium cetyl sulphate per litre. The method is fully described and there is a clear photograph of the apparatus used. J. W. D.

**Measurement of Characteristic Wetting Values. Introduction of these Values into Some Practical Problems.** I. J. Guastalla, L. P. Guastalla, and H. L. Rosano. *Bull. mens. ITERG (Inst. Corps gras)*, **6**, 60–68 (1952): *Chem. Abs.*, **46**, 4320 (25 May 1952).

Terms used in determining wetting properties of solutions are defined. A tensiometer which enables simultaneous determination of surface tension, adhesion tension, and, indirectly, of contact angles, interfacial forces, etc. has two blades dipping into the liquid and connected with a recording mechanism. C. O. C.

**Polarographic Estimation of Some Phenylmercuric Compounds.** V. Vojíř. *Congress of Practical Polarography* (Bratislava and Prague: Central Polarographic Institute, 18–19 Feb. 1952): *Anal. Chem.*, **24**, 915 (May 1952).

Phenylmercuric compounds, in which the bivalent mercury is joined to the carbon atom by a chemical bond, are reduced at the dropping mercury electrode in two one-electron steps. The electroreduction proceeds via a free radical, which dimerises after its formation and crystallises at the electrode surface. This crystallisation causes irregularities in the diffusion current. The formation of the precipitate at the electrode and its effects were studied by the aid of microscope and current–time curves. In the second reduction step the C–Hg bond is split to form free mercury and an aromatic hydrocarbon. C. J. W. H.

**Qualitative Detection of Long-chain Alkylpyridinium Halides.** E. G. Brown. *Analyst*, **77**, 211 (April 1952).

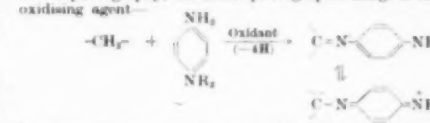
A drop of saturated aqueous sodium 1:2-naphthaquinone-4-sulphonate is mingled with one drop of test soln. on a drop reaction paper. On rendering alkaline with one drop of 0·5 *N*-NaOH, a red-violet colour concentrates round the centre of the spot when an alkylpyridinium halide is present. When it is present in larger quantities the colour diffuses outwards. Amounts of Fixanol VR (cetylpyridinium bromide) as small as 25 μg. at concn. as low as 1 in 2000 can be identified. The test may be applied to the detection of such substances on textile materials. J. W. D.

**Determination of Primary Aromatic Amines by Diazotisation using the Dead-stop End-point.** H. G. Scholten and K. G. Stone. *Anal. Chem.*, **24**, 749–750 (April 1952).

The acidified amine soln. is titrated with $NaNO_2$ soln. (standardised against sulphanilic acid) in presence of KBr as catalyst; a potential of 0·4 v. is applied between two Pt electrodes. Under these conditions a current flows when $HNO_2$ equiv. to 0·05 ml. of 0·1 M-$NaNO_2$ soln. is present in 200–400 ml. of reaction soln. The method, which is described in full, is claimed to have the following advantages—(1) loss of $HNO_2$ is minimised, (2) analysis is carried out at room temp., at which reaction rate is comparatively rapid, (3) use of KBr minimises time spent in vicinity of end-point, and (4) no external indicator is needed. J. W. D.

**Test for Highly Active Methylene Groups.** P. F. Warfield. *Anal. Chem.*, **24**, 890–891 (May 1952).

In the following reaction, which is the basis of modern colour photography, the latent photographic image is the oxidising agent—




If an oxidising agent such as sodium ferricyanide or potassium persulphate is used the reaction may be employed to detect colour formers containing highly active methylene groups. Unless it has two powerful electron-attracting groups attached (e.g. CN, CO·R, COOH), an active methylene group will not react, but if it is part of a 5- or 6-membered ring one activating group may suffice. The more electronegative the activating groups the more bathochromic is the shift in the absorption of the dye formed. The test, which is described in full, employs *p*-diethylaminoaniline as reagent, and requires only ca. 1 mg. of the unknown. Compounds responding to the test may be classified according to the colour produced—

| | |
|---|---|
| Blue–green ... ... | Phenols and naphthols |
| Red–violet ... ... | Cyanoacetyl compounds and 5-pyrazolones |
| Yellow–orange... ... | 1:3-Carbonyl type |

Colour developers (e.g. dialkylaminoanilines) may be quantitatively estimated with an accuracy of ± 5% by using known colour formers. J. W. D.

**Spectrographic Method for the Detection of Active Methylene Groups.** A. Bruylants, E. Braye, and A. Schonne. *Helv. Chim. Acta*, **35**, 1127–1139 (June 1952).

A spectrographic method is described which enables the prediction of the reactivity of a cyanomethyl group towards aldehydes in the presence of a base acting as catalyst, and which consists in measuring the absorption spectra of a nitrile in neutral and alkaline solutions. If there is a shift in the latter with respect to the former to longer wavelengths (bathochromic effect), or to lower values of transmission (hyperchromic effect), or if both effects appear together, then the nitrile has ionised in the alkaline medium and will react with a suitable carbonyl compound; if both spectra are the same, or lie very near each other, then the nitrile is inactive. The mechanism of the reaction is discussed, its validity checked on the reactions of nine nitriles with benzaldehyde and *p*-dimethylaminobenzaldehyde, and the method claimed to be general for the detection of the reactivity of both methyl and methylene groups in their ionic reactions. H. H. H.

**Fluorescence Analysis in Ultraviolet Radiation.** J. A. Radley. *Lab. Practice*, **1**, 24–29 (April), 67–72 (May), 114–117 (June 1952).

A review of techniques and apparatus under headings which include chromatography, fluorescence microscopy, secondary fluorescence, reactions yielding fluorescent end-products, and fluorescent indicators in volumetric titrations. Materials to which the applications of these techniques are discussed include textile and papermaking fibres (including differentiation between the various rayons), dyes, and tanning agents. Fluorescent indicators may be used in the acidi- or alkali-metric titration of dark liquids such as spent kier liquor, and in the titrimetric determination of sol. chlorides, e.g. NaCl as diluent in commercial dyestuffs. J. W. D.

**Preparing Pigment Samples for the Electron Microscope.** G. D. Sogare. *Chimica e Industria* (Milan), **33**, 546–548 (1951); *Chem. Abs.*, **46**, 5334 (10 June 1952).

When drying a drop of pigment dispersion to obtain a powdered sample for electron microscopy, agglomeration of particles often makes observation difficult. This can be avoided by blowing warm, dry air under vacuum over the powder to be examined, picking up a small portion, and depositing it as a film on a specimen slide. A detailed drawing of the bulb in which the powder is placed is given. C. O. C.

**Analysis of Organic Pigments.** K. G. Hargreaves. *J. Oil & Col. Chem. Assocn.*, **35**, 139–161 (April 1952).

Pigments can be classified into the following four groups: azo pigments, lakes and toners of acid dyes, lakes of basic dyes, vat and other products. The reduction of azo compounds of the first two types, with sodium hydrosulphite under various conditions, and the isolation and identification of the scission products are described. Other methods of breaking down azo compounds, such as distillation with soda lime or sodium dihydrogen phosphate, hydrolysis with strong sulphuric acid, and scission with fuming nitric acid to give a diazonium nitrate, are also mentioned. The spot reactions of all types of pigments with conc. $H_2SO_4$ and alcoholic KOH are tabulated as a method of rapid identification of dyes most frequently used commercially. A very brief account is given of methods of separating mixtures. C. H. R.

**Determination of Adhesiveness of Printing Inks.** V. I. Zolotnitsky, B. N. Shakhkeldyan, and E. S. Popkova. *Poligraf. Proizvodstvo*, (11), 25–26 (1951); *Chem. Abs.*, **46**, 4811 (25 May 1952).

The adhesive tendency of the ink is measured by allowing a small roller mounted on a slide attached to a spring balance to contact a wheel whose surface is coated with the ink and which is rotated by a standard motor. The pull on the roller at a given velocity of the wheel is translated in terms of adhesiveness of the ink. Typical curves are given. C. O. C.

**Colorimetric Determination of the pH of Cotton Fibre.** W. A. Pons and C. L. Hoffpauir. *Text. Research J.*, **22**, 200–202 (March 1952).

A colorimetric method using neutralised sulphonphthalein indicators for the determination of the pH of cotton fibre is described. A standard deviation of 0·17 pH unit was obtained compared with an electrometric method. A. B.

**Characterisation of Cellulose by Hydrolysis.** W. E. Roseveare. *Ind. Eng. Chem.*, **44**, 168–172 (Jan. 1952).

The specific reaction rates for the solution of the reactive fractions of various native and regenerated celluloses, on hydrolysis in dil. $H_2SO_4$, were found to be the same. The degree of polymerisation after hydrolysis is a suitable means of characterising different types of cellulose and showing up the changes produced by treatment with various NaOH concentrations. Crystallisation of amorphous cellulose on hydrolysis is inhibited by prior oxidation, and thus it may be removed entirely on subsequent hydrolysis. W. K. R.

**Rapid Method for Determining Cuprammonium Viscosity.** M. Rutishauser and A. Weber. *Svensk Papperstidning*, **55**, 67–71 (15 Feb. 1952); H. Doering; M. Rutishauser. *Ibid.*, **55**, 406–407 (15 June 1952).

The combined addition of a wetting agent and pyrogallol to the TAPPI viscosity tube allows the dissolving time for the usual qualities of cellulose to be reduced to 5–10 min. The cuprammonium solution is prepared according to the TAPPI method, and to every litre 2 g. sucrose and 1 ml. Invadin JFC 100% (a wetting agent) are added. The test is carried out as laid down by TAPPI, except that two drops of 50% pyrogallol solution are added to the practically full viscometer tube. The latter is placed in the thermostat after 5–10 min. mechanical agitation.

Doering contends, from experimental work on pulp viscosity determinations with and without nitrogen, that brief contact of the solution with air has little or no effect and may be ignored in rapid methods, and that inaccuracies in the weight of the initial pulp sample are common to all methods. In his reply Rutishauser insists that air must be excluded from the solution, and extreme accuracy is needed in conditioning and weighing the pulp sample and in maintaining the correct temperature in the thermostat during the test. S. V. S.

**Tentative Method for Determination of Viscosity of Cellulose dissolved in Cupriethylenediamine.** K. Wilson. *Svensk Papperstidning*, **55**, 125–133 (29 Feb. 1952).

The pulp is defibrated in 25 ml. of water in a 50-ml. bottle, together with some pieces of Cu, and is then dissolved by adding 25 ml. of 0·4 N. cupriethylenediamine and shaking for 15 min. The viscosity is determined in a Wagner–Russel viscometer at a velocity gradient of 200 $sec.^{-1}$, or in an ordinary pipette viscometer and the viscosity recalculated to the gradient specified with the aid of a curve. S. V. S.

**Calculation of the Molecular Weights of Various Cellulosic Materials from the Velocity Constants for Sedimentation or Diffusion.** B. A. Zakharov. *Doklady Akad. Nauk S.S.S.R.*, **81**, 629–631 (1 Dec. 1951).

Sedimentation and diffusion data for solutions of various preparations of cellulose in cuprammonium soln. are collected from the literature, and the mol. wt. $M$ of these materials are calculated from the general formula applying to macromolecular substances, which involves both the sedimentation const. $S_0$ and the diffusion const. $D_0$. It is now shown that for cellulose empirical equations can be set up, viz.—

$$M = 9{\cdot}20.10^{4}D_0^{-1.88} \text{ and } M = 9{\cdot}46.10^{8}S_0^{2.248}$$

which enable mol. wt. to be determined with good accuracy from diffusion data only or from sedimentation data only. A. E. S.

**Simple Mechanical Means of Judging Handle.** A.A.T.C.C. South Central Section. *Amer. Dyestuff Rep.*, **41**, P 167–P 172 (17 March 1952).

Several mechanical contrivances for measuring handle of yarns and fabric are discussed. Most promising is one in which the tension necessary to pull a piece of material through a pot-eye is measured. J. W. B.

**Qualitative Reaction for Lignin.** S. N. Bekétovsky. *J. Anal. Chem. U.S.S.R.*, **6**, 328 (Sept.–Oct. 1951).

Lignin-containing material shows a yellowish-green coloration when spotted with a soln. of $H_2S$ in dil. HCl (e.g. a saturated soln. in 2 N. acid) and then dried. Pure cellulose gives a yellowish-orange coloration. A. E. S.

**Determination of Lignin in Jute.** W. G. Macmillan, A. B. Sen Gupta, and A. Roy. *J. Textile Inst.*, **43**, T 103–T 111 (March 1952).

Treatments with 72% $H_2SO_4$ on partly delignified jute containing a higher proportion of xylan show that the time for obtaining the optimum yield of lignin, and the rate of formation of condensation product, are almost the same as those of raw jute. Preliminary hydrolysis with dil. acid removes a portion of lignin not only from raw jute but also from partly delignified samples, thereby increasing the yield. Comparative study of lignin contents determined at 2° and 22° C. show that at 22° C. the increased yield of lignin, in presence of xylose or xylan, is due to furfural–lignin complexes which are not formed at 2° C. Elimination of this side-reaction by a preliminary hydrolytic treatment simultaneously removes a portion of the lignin. However, use of cold 72% and boiling 3% acids isolates a lignin contaminated with some non-ligneous matter; an accurate result is obtained by a combination of positive and negative errors. A rapid determination, therefore,

involves treating with 72% $H_2SO_4$ for 45–60 min. at 22° C., diluting to 3%, refluxing for 2 hr., and weighing the insol. residue. J. W. B.

**Determination of Carbon Disulphide in the Atmosphere.** J. Heyrovsky. *Congress of Practical Polarography* (Bratislava and Prague: Central Polarographic Institute, 18–19 Feb. 1952): *Anal. Chem.*, **24**, 915 (May 1952).

Carbon disulphide has been found to give well defined polarographic waves in practically all electrolytes. For the analysis of air a 10% solution of sodium sulphite is recommended, as it absorbs oxygen and shows only the two waves due to carbon disulphide. The first of these occurs at the applied voltage of 1·0 v., and the second, which is somewhat smaller, appears at 1·4 v., coinciding with that of formaldehyde. Air is slowly passed through the sulphite solution placed in a special 1-ml. microvessel, being sucked by a small turbine. The quantity of 1 $\mu$g. of carbon disulphide in 1 ml. is distinctly shown. With the same sensitivity the depolarisation effect of carbon disulphide is also shown oscillographically. These, as well as the polarographic effects, are different from those of hydrogen sulphide. C. J. W. H.

**Fibre Cross-sections.** K. Makishima. *J. Soc. Textile Cellulose Ind.* (Japan), **6**, 183–185 (1950): *Chem. Abs.*, **46**, 4802 (25 May 1952).

Nylon, vinylon, or viscose staple embedded in cellulose nitrate in a 2 : 3 mixture of methyl alcohol and ether is easily cut into sections 3–4 $\mu$. thick. The sections keep well in 70–80% aq. methyl alcohol. C. O. C.

**Quantitative Microscopic Estimation of Fibres in a Blended Yarn.** H. Cirr. *Melliand Textilber.*, **33**, 448–449 (May 1952).

Blended yarns are examined under the microscope, and the relative numbers ($n_1$, $n_2$, . . .) and average diameters ($d_1$, $d_2$, . . . in arbitrary units) of the various fibres are determined. The relative weights of the fibres present in the blend are then given by $d_1^2n_1\rho_1 : d_2^2n_2\rho_2 : \ldots$ ($\rho_1$, $\rho_2$, . . . = densities of the fibres). A. E. S.

**Interlaboratory Study on Determination of Acetyl in Cellulose Acetate.** American Chemical Society, Progress Report by Subcommittee on Acyl Analysis, Division of Cellulose Chemistry Committee on Standards and Methods of Testing. *Anal. Chem.*, **24**, 400–403 (Feb. 1952).

Two samples of commercial cellulose acetate were analysed (using the Eberstadt method) by nine laboratories, and in each laboratory two workers analysed each sample in duplicate on three different days. Agreement between duplicates and operators in each laboratory was found to be good, but amongst the separate laboratories it was not satisfactory. Though deviations from and variations in the procedure accounted for some large deviations, others remained unexplained. The method is proposed as a standard. J. W. D.

**Time of Recovery from Supercontraction as an Indication of the Degree of Damage in Wool Fibres—A Suggested New Test.** M. Z. Rzegocinski and R. Lund. *J. Textile Inst.*, **43**, T 91–T 102 (March 1952).

Wool fibres are cut to a length of 120–150 $\mu$. and immersed in a drop of Krais–Viertel–Markert (K.V.M.) reagent (ammoniacal KOH) on a microscope slide. Length changes are observed by means of a projection microscope (× 500), and plotted on paper by tracing. Undamaged fibres supercontract, return to their original length, and then extend; the time taken to recover the original length is known as the recovery time (RT). RTs for untreated 70s, 58s, and 50s fibres are studied, and also for 70s fibres modified by alkali (NaOH), light (Fadeometer), dry heat, boiling in water and buffers of pH 5 and 6, boiling in formic acid, acid dyeing, and metachrome and after-chrome dyeing. Kiton Red, Indigo Carmine, and alkali solubility tests are carried out. Clear distinction is possible between acid-damaged fibres and those damaged by alkali, light, heat, or boiling water, and the magnitude of the RT can also be used as a measure of the degree of modification. Co-ordination with other tests is necessary if further distinction is required. J. W. B.

**Alkali Solubility Test for Determining the Degree of Fibre Damage in Wool.** K. Lees and F. F. Elsworth. *J.S.D.C.*, **68**, 207–213 (June 1952).

**Measurement of Damage produced by Treatment of Wool with Solutions of Hydrogen Peroxide.** G. Laxer and C. S. Whewell. *J.S.D.C.*, **68**, 256–257 (July 1952).

**Identification of Synthetic Fibres.** H. M. Ulrich. *Textil-Praxis*, **7**, 150–154 (Feb.), and 211–215 (March 1952).

A detailed scheme for the identification of synthetic fibres under the following headings—Physical appearance, microscopical examination, sp. gr., effect of dry distillation, fluorescence in ultraviolet radiation, identification of organic radicals, saponification with alcoholic potash, staining tests, tests giving specific colour reactions, papyrographic analysis, solubility in inorganic and organic compounds with particular reference to the differentiation of superpolyamides (nylon 66, Perlon L, and Grilon), differentiation of American nylon and German Perlon L by m.p., differentiation of high-polymer fibres by contraction temp. and m.p. using Preston's copper block method, and characterisation of synthetic fibres by their thermal behaviour in hot media. B. K.

**"Zillo Test"—Apparatus for Identifying Synthetic Fibres.** H. Zill. *Melliand Textilber.*, **33**, 453–454 (May 1952).

The "Zillo" test is a set of apparatus and solvents supplied for use in the identification of a synthetic fibre. Samples of the fibre under test are treated with each of seven solvent mixtures, the precise compositions of which are not given. The solvents are numbered 1–7, and are tried in that order until a solvent that dissolves the fibre is found. The fibre is accordingly allotted to one of seven groups, and, for the synthetic fibres available at present, these groups are found to follow a classification based on chemical constitution. A. E. S.

**Quantitative Analysis of Nylon, Perlon, and Vinyon in Mixture Yarns.** M. Antoniotti. *Mondo tessile*, **3**, 284–288 (1948): *Chem. Abs.*, **46**, 2808 (25 March 1952).

Nylon is determined in a mixture with Perlon (either as a mixed-fibre yarn or as a copolymer) by boiling the sample with 30% $H_2SO_4$ for several hr., when adipic acid formed from nylon is isolated while Perlon is converted into soluble products. A correction factor is used for the loss of 6–7% adipic acid. Mixtures of natural and synthetic fibres are analysed by dissolving out the polyamide fibres by shaking with a cold solution of $CaCl_2$ in 20% methyl alcohol and reprecipitating them by pouring the filtrate into a large volume of cold water, the dried precipitate is then analysed for nylon and Perlon as above. The residual fibre mixture is treated with cold 85% formic acid to dissolve the acetate rayon. Vinyon is dissolved with acetone; the remaining fibres are analysed by the usual methods. Correction factors are used for the slight loss of non-polyamide factors dissolved out by the $CaCl_2$ solution. An eight-fibre mixture can be analysed with reasonable accuracy. C. O. C.

**Comparative Study of Fungal-resistance Tests in Specifications involving Cotton Goods.** J. V. Harvey. *Office of the Q.M. General, Microbiology Series Report* 14* (April 1949). Pp. 43.

A review of specified fungal-resistance tests for cotton goods, supplied under U.S. Government contract, with a view to standardising test procedure and economising in testing time and materials used, recommendations being made to that end. C. O. C.

*Available from T.I.D.U., D.S.I.R., Cunard Building, 15 Regent Street, London S.W.1.

**Testing the Fungal Resistance of Plastic-coated Fabrics and Plastics Films.** E. Rolle. *Q.M.G. Research Report, Microbiology Series Report* 13* (no date). Pp. 13.

Flexibility changes are used to measure the extent of fungal or bacterial deterioration. The tests are reproducible with a high degree of precision. C. O. C.

*Available from T.I.D.U., D.S.I.R., Cunard Building, 15 Regent Street, London S.W.1.

**Studies on the Degradation of Plastic Films and Coatings by Fungi and Bacteria.** J. V. Harvey and F. A. Meloso. *Q.M.G. Lab. Microbiology Series Report* 16* (Aug. 1949). Pp. 54.

*Aspergillus versicolor* was used as the test organism on a

large number of vinyl and polyvinyl butyral films and coated fabrics using various plasticisers. Stuffness of the film after attack was used as the criterion of the damage done. C. O. C.

*Available from T.I.D.C., D.S.I.R., Cunard Building, 15 Regent Street, London S.W.1.

**Method for Predicting Dye Penetration on Leather.** W. K. Schweitzer and R. M. Lollar. *J. Amer. Leather Chem. Assocn.*, **47**, 140–151 (March 1952).

Samples of chrome-tanned calf leather, taken from the bend area of the skin, soaked in a pH 4 buffer and subsequently treated with a dil. quebracho soln., are dyed under standard conditions with a large number of acid, basic, and direct dyes. The degree of penetration of the dyes is measured microscopically, and the capillary rise of the dyes on quebracho-mordanted filter paper is also measured. It is found that capillary rise varies approx. linearly with the logarithm of the penetration. A. J.

**Apparatus for Measuring the Colour Fastness of Light Leathers to Wet and Dry Rubbing.** G. R. Nave. *J. Soc. Leather Trades Chem.*, **36**, 15–19 (Jan. 1952).

The apparatus consists of a brass drum, of 3 in. radius, driven at 5–20 r.p.m., and covered with white cotton tape. The leather sample is mounted on a brass block, held in a vertical slide, in contact with the drum at its highest point and pressed on to the drum by a suitable load. Suggested loads are 2000 g. for dry tests and 300 g. for wet tests. The drum is rotated until the first trace of colour appears on the tape, and log (number of revolutions × 100) is designated the "rub number". Considerable differences in the rubbing fastness of visually similar leathers are observed. A. J.

PATENTS

**Measuring the Thickness of Transparent Sheets with the Aid of an Interferometer.** Celanese Corpn. of America. *BP* 672,486

**Measuring Extension under Tension of Rubber.** ICI. *BP* 673,203

The motion of two points on a sample of rubber which is being stretched is transmitted by levers to two sliding-contact assemblies. While sliding, each of these operates repeatedly a make-and-break in an electrical circuit, energising an electromagnet which drives a ratchet wheel through an armature and pawl. The difference in motion of the two ratchet wheels is utilised as a measure of the extension of the sample. J. W. B.

**Electrical-resistance Thermometers.** Foxboro Co. *BP* 673,609

**Diaphragms for Phase-contrast Microscopes.** Hilger & Watts. *BP* 673,861

[Acid–Base Indicators from Diazotised] 4-Nitro-4′-aminodiphenyl Sulphone (IV p. 315).

Polarographic Investigation of the Redox Behaviour of Certain Hydroxy and Sulphonic Acid Derivatives of Anthraquinone (IV p. 317).

Chemical Changes produced in the Cellulose Macromolecule by Oxidising Agents. IV—Lactone Linkages in the Oxycellulose Macromolecule and their Effect on the Estimation of Carbonyl Groups by the Hydroxylamine Condensation Method. V—Proof of the Existence of α-Hydroxymonoketone Groups in Oxycelluloses. VI—Presence in Oxycelluloses of Carbonic Ester Groupings and their Effect on the Estimation of Uronic Carboxyl Groups (XI p. 329).

## XV MISCELLANEOUS

**Safety and Industrial Hygiene in the Laboratory.** H. H. Fawcett. *Chem. Eng. News*, **30**, 2588–2591 (23 June 1952).

Accident prevention in laboratories can be secured by (1) planned facilities, (2) proper equipment, and (3) continued education, examples of how each may contribute to the desired end being given. C. O. C.

**Dichroism in Stretched Films.** W. Hanle and H. Scherer. *Z. Naturforsch.*, **6a**, 437–439 (1951); *Chem. Abs.*, **46**, 2880 (10 April 1952).

Dichroism can be obtained in stretched colloidal films, e.g. regenerated cellulose, in any desired spectral region by the use of various dyes. Ranges for 157 dyes with which polarisation is found between 250 and 590 mμ. are given. C. O. C.

**Photochemical Transformation of Ammonium Nitrite—I. II—Effect of Fluorescent Dyes.** N. R. Dhar and C. V. Suryanarayana. *Proc. Natl. Acad. Sci. India*, **19 A**, 1–5, 114–139 (1950); *Chem. Abs.*, **46**, 2946–2947 (10 April 1952).

**I**—Exposing dil. aq. $NH_4NO_2$ to sunlight for 50 hr. at a mean temperature of 49·5°C. in presence of either $TiO_2$ or $SiO_2$ results in increase of both decomposition to $N_2$ and $H_2O$ and oxidation to $NH_4NO_3$. Under identical conditions in the dark there is little oxidation but some decomposition. Presence of $TiO_2$ results in more decomposition and oxidation than does $SiO_2$.

**II**—Eosin, Acridine Orange, Erythrosin, chlorophyll, uranyl acetate, Rhodamine BS, and succinylfluorescein promote the oxidation and retard decomposition in presence of $SiO_2$ or $TiO_2$. More fading of the dye occurred in presence of $TiO_2$ than $SiO_2$. In general the more stable the dye the more it promoted oxidation. C. O. C.

PATENTS

**Staining of Histological Tissue Specimens.** Technicon Chemical Co. *BP* 673,441

A stain for use in the microscopic examination of animal tissues contains a staining agent, e.g. oxidised hæmatoxylin or eosin, and a mordant, e.g. Ca acetate and $CrO_3$, the amounts of staining agent and mordant being those of their equivalent chemical combining weights. There is also present a buffer of pH 3·0, and when hæmatoxylin is present a solvent, e.g. diethylene glycol, which inhibits further oxidation. C. O. C.

**Modifying the Spectrum emitted by an Artificial Light.** P. Malifaud. *BP* 671,687

A light source is arranged within a reflector which reflects only part of the emitted spectrum and which directs all reflected rays back through the source, thus effecting a blend while maintaining a point source. For example, a bluish-violet reflecting surface, used with an ordinary incandescent bulb, finally emits white light. J. W. B.

**Preservation of Pigments in Dried Vegetable Matter.** National Alfalfa Dehydrating & Milling Co. *BP* 672,799

The colour of grass and other vegetable matter is preserved when it is dried if it is first treated with a tissue-penetrating light mineral or vegetable oil of low volatility in which has been dissolved a monoalkoxy-, monohydroxy-, or monoanilino-diphenylamine. C. O. C.

**Coating Aluminium and its Alloys.** American Chemical Paint Co. *BP* 673,677

The metal is treated with an aqueous solution at pH 3·2–7·0 containing "$CrO_3$" ions (dichromate) (3·2–140·0 g. per litre), phosphate ions (1·5–300·0), and fluoride ions (0·75–95·0). There are 0·17–2·6 fluoride ions per $CrO_3$ ion. This gives an excellent basis for paints and other finishes, and is a very efficient protection against corrosion. C. O. C.

**Coating Copper or its Alloys with an Ancient Green Patina.** M. Quadrio. *BP* 671,862

The article is dipped first in aq. $K_2S$ and then in aq. $H_2SO_4$, dried, and then repeatedly dipped in aq. sal ammoniac, being dried between each immersion until the desired effect is obtained. It is then coated with an alcoholic solution of shellac, and finally with a clear cellulose nitrate lacquer. C. O. C.

**Blackening Iron and Steel and their Alloys.** I. L. Newell. *USP* 2,579,752

Treatment in boiling dilute aqueous solution of a salt of an arylsulphonemonochloramide made alkaline with an alkali-metal hydroxide is very effective. C. O. C.

**Coloured Granules for Decorating Building Materials.** Monsanto. *BP* 672,683

Mineral granules, e.g. crushed slag, are coloured by mixing them with an aqueous solution of an orthophosphate and a pigment, and then heating the product to convert the orthophosphate to the metaphosphate and so bond the pigment to the surface of the granules. C. O. C.

# SITUATIONS VACANT AND WANTED, Etc.

Replies may be addressed "Box —, Society of Dyers and Colourists," Dean House, 19 Piccadilly, Bradford, Yorks., where all communications relating to these Advertisements, which are treated in strict confidence, should be addressed.

The Publications Committee is prepared to receive Advertisements relating to Situations Vacant, Situations Wanted, or Miscellaneous Items for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

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## SITUATIONS VACANT

CHEMIST, preferably with B.Sc. or Ph.D. to build up and control a new technical service laboratory on Tyneside. He must be familiar with the dyeing and wet processing of textiles and with the properties of textile auxiliary products. The appointment includes investigation and liaison work and will prove to be interesting and offer unlimited scope to the man who can accept responsibility, and combine technical knowledge with commercial outlook. Written applications, which will be treated in strict confidence, must give full particulars of qualifications, industrial experience, age and salary required to Managing Director. Box V582

EXPERIENCED DYER of rayon and cotton piece goods, with a knowledge of chemistry, required for a dyehouse in Egypt. State age and experience. Box V584

FOR INDIA. Chemists wanted for Cotton and Woollen Mills in South India, under British Management. Minimum qualification University degree or equivalent.

Good salaries on a rising scale are offered according to age and capabilities of applicants. In addition to salary a substantial "cost of living" allowance is paid monthly.

Other amenities are — free furnished quarters, free medical attention, provident fund, superannuation fund, home leave with free passages for the officers and their wives. First contract for three years.

Apply, stating age, qualifications, whether married or single, and giving details of any family, to Binny & Co. Ltd., 122 Leadenhall Street, London E.C.3.

LARGE Dyeing, Printing and Finishing Works in Lancashire has vacancies for chemists in the research laboratories. For one of the posts, candidates should have a good degree and several years' experience in work of a similar type; age preferably 30–35. For another post, a younger man with a good degree would be suitable; knowledge of dyestuffs and textile fabrics desirable but not essential. Salary according to qualifications and experience; Pensions Scheme. Box V580

LEADING Hosiery Manufacturers require Assistant Chemist for Dyeing and Finishing Departments. Age 25–30. Laboratory experience and some knowledge of Textile Fibres essential. Write, giving details of previous details, to Box V581

MANCHESTER MUNICIPAL COLLEGE OF TECHNOLOGY

THE Governing Body invites applications for the appointment of a FULL-TIME TEACHER IN THE DEPARTMENT OF TEXTILE CHEMISTRY.

Applicants should have had practical experience of Dyeing, Printing and Finishing in order to be able to operate these processes in the College Dyehouse and to give practical instruction to students, and should possess a City and Guilds of London Institute Full Technological Certificate in Dyeing of Cotton or Textile Printing (or equivalent).

Salary scale—£450 per annum, rising by annual increments of £25 to £725. Subject to this maximum not being exceeded, one increment of £18 will be added to the minimum in respect of each year of approved industrial experience up to a maximum of 12, together with one further increment (usually of £18) for each year of previous full-time teaching service. There are also certain additional training and graduate allowances.

A form of application may be obtained from The Registrar, College of Technology, Manchester 1. The last date for the receipt of applications is 1st *September* 1952.

Canvassing, either directly or indirectly, will disqualify a candidate for appointment.

D. CARDWELL, Acting Principal.

TECHNICAL Representative required with knowledge of dyestuffs and Auxiliaries for the Yorkshire area. Box V583

W. E. SAXBY (Leicester) LTD. have vacancy in laboratory for a Textile Chemist with works' experience, capable of carrying out research programme and supervising routine testing.

## MISCELLANEOUS

ONE Mercerising Range, complete with circulating pump. Length of clips 60 ft. By Mather & Platt Ltd. Mangle not included. This machine is in very good order.

ONE Three Bowl White Mangle, two wood, one brass, complete with Scutcher. This can be sold as a whole unit or as separate lots. This machine is in very good order.

WANTED—Copy of bound volume on Symposium on Fibrous Proteins. Box M448

## ADDRESSES WANTED

Evelbauer, H. L., formerly of Friedrichsster 7, Marburg (16), Hessen, U.S. Zone, Germany.

Josephson, C., formerly of c/o Silknit Ltd., 400 Sidney Road, Durban, South Africa.

Justice, A., formerly of 35 Cumberland Avenue, Liverpool.

Lowe, R., formerly of 17 Ashdown Avenue, Leicester.

MacCallum, J. C., formerly of The Lace Research Association, 71 Upper Parliament Street, Nottingham.

Marriott, F. W., formerly of 49 Woodcot Avenue, Baildon, near Shipley.

Thitchener, C. R., formerly of 29 Moorland Avenue, Leeds 6.

# Notice to Authors of Papers

The MSS. of all papers communicated to or read before the Society become the property of the Society. They should be addressed to the Editor, Society of Dyers and Colourists, 19 Piccadilly, Bradford. Authors must not allow their papers to be published elsewhere before they have appeared in the Society's *Journal*. Should prior publication take place without the sanction of the Publications Committee, the paper will be printed only as an abstract or summary.

Manuscripts submitted for publication in the *Journal* should be typewritten (double spacing) on good-quality paper, using one side of the paper only and leaving a margin at least 1 in. wide on the left-hand side. The time taken in refereeing papers (both lectures and communications) will be reduced to a minimum when authors submit two copies of the typescript.

In view of the high costs of publication, it is essential that authors should be as concise as possible. When experimental procedure has already been published, a literature reference to the paper containing the details is sufficient, whilst well known experimental methods should be described very briefly.

Introductory paragraphs describing the aims of the investigation and the method of attack are desirable, and should be followed by the experimental results and their discussion. There should be a brief summary for insertion at the beginning of the paper. References to the literature should be numbered consecutively, using superscript numbers without brackets immediately following the text words or author's name to which they refer.

The list of references should be given at the end of the manuscript and the abbreviations used should be, as far as possible, those given in the "List of Periodicals Abstracted" included at the end of the Index to the preceding year's *Journal*. Reference numbers in this list should be neither enclosed in brackets nor followed by full-stops. As far as possible throughout the manuscript the abbreviations listed in the Jan. 1950 issue (p. 54) should be used. Tables should be numbered consecutively in Roman numerals and Figures in Arabic numerals.

The number of figures and graphs should be kept as low as possible, and data should be presented in the form of either tables or graphs, not both. Drawings should be carefully prepared, preferably in Indian ink, on plain white drawing paper or, preferably, Bristol board. In graphs, the frame and actual curves should be ruled and inked more heavily than any co-ordinate lines, and the latter should not be close together as in ordinary graph paper. Experimental points should always be given, and where several graphs appear in a single Figure clear means of differentiation must be adopted. All numbers and legends are set up in type by the printer, and authors should therefore indicate them lightly in pencil.

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